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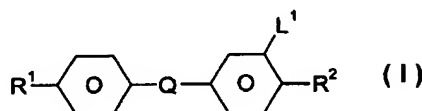
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(54) Title: POLYMERIZABLE, LUMINESCENT COMPOUNDS AND MIXTURES, LUMINESCENT POLYMER MATERIALS AND THEIR USE



(57) Abstract: The invention relates to new polymerizable, luminescent compounds of formula I wherein R¹, R², Q and L¹ have the meanings given in claim 1. Furthermore the invention relates to polymerizable mixtures containing compounds according to the invention and preferably at least one polymerizable mesogenic compound. Polymer materials obtainable by polymerizing such mixtures are also described. These compounds, mixtures and materials show advantageous photoluminescent and/or electroluminescent properties and may be used in light emitting devices and optical- or electrooptical display elements.

WO 2004/003102 A2

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**Polymerizable, luminescent compounds and mixtures,
luminescent polymer materials and their use**

Field of Invention

5 The invention relates to polymerizable, luminescent compounds, to
polymerizable mixtures comprising such compounds and to luminescent
polymer materials obtainable by polymerizing such compounds or
mixtures. Furthermore the invention relates to the use of these compounds
and mixtures for the manufacture of photoluminescent and/or
10 electroluminescent polymer materials. The invention also relates to the use
of these polymer materials as photo- and/or electroluminescent materials
in light emitting devices, optical and/or electrooptical display elements.
Additionally the invention relates to light emitting devices and optical or
electrooptical display elements comprising these polymer materials.

15

Background and Prior Art

20

Luminescent polymers showing photoluminescence as well as polymers
showing electroluminescence were proposed to be used in light emitting
devices and electrooptical display elements.

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The organic light emitting devices or diodes (OLEDs) currently being under
intense research consist of at least one emission layer. Common OLEDs
are realized using multilayer structures, where an emission layer is
sandwiched between one or more electron-transport and/or hole-transport
layers. By applying an electric voltage electrons and holes as charge
carriers move towards the emission layer where their recombination leads
to the excitation and hence luminescence of the lumophor units contained
in the emission layer. The sandwich structure is built by vacuum deposition
or spin coating techniques which may include a polymerization step before
applying the next layer (Meerholz et al., Synthetic Metals 111-112 (2000)
31-34). OLEDs which are available in different colors have the potential of
being used as the building blocks of different kind of information displays.

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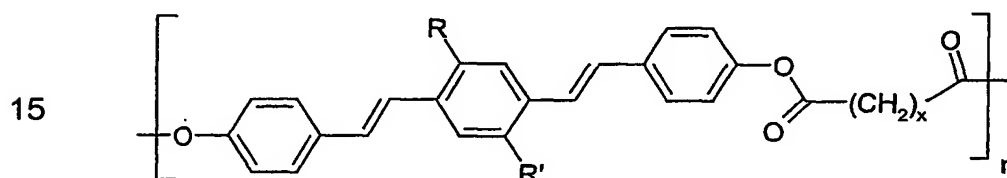
Also anisotropic luminescent polymers are known where the polymer and/or the lumophor units are oriented. These emissive materials show anisotropic absorption and/or anisotropic emission of polarized light. The degree of absorption and/or emission of linearly polarized light depends on the relative orientation of the wavevector to the main director of the fluorophor molecules. Such an orientation within the luminescent materials can be achieved by different methods:

- incorporation of luminescent molecules into an oriented polymer prior or after the orientation step,
- tensile orientation of a ductile luminescent polymer (e. g. the techniques described in WO 00/07525),
- rubbing of the luminescent polymer,
- applying the Langmuir-Blodgett technique,
- oriented growth of the luminescent materials onto oriented substrates, like onto known alignment layers,
- polymerization of oriented liquid crystals,
- photo-induced alignment,
- alignment in electric, magnetic or flow fields.

By using their anisotropic optical characteristics, these materials can replace polarizers and/or color filters which reduce the light efficiency in liquid crystal displays (LCDs) by up to 80% and more. Hence display devices employing such anisotropic luminescent polymers are described to show a high brightness and contrast, and furthermore a good viewing angle (Weder et al., Science 279 (1998), 835 and EP 889 350 A1). Using pixel elements of at least three different photoluminescent materials multicolor images may be displayed. In major embodiments of such display devices an anisotropic photoluminescent layer substitutes the polarizer of a conventional backlight – polarizer – light valve – polarizer arrangement, where the light valve uses known electrooptical effects of liquid crystal materials, like the TN- or ECB-effect. A high degree of polarized emission is necessary in embodiments where the photoluminescent layer is arranged directly behind the backlight. Whereas a high degree of polarized absorption is mandatory in devices where the photoluminescent layer is placed behind the light valve.

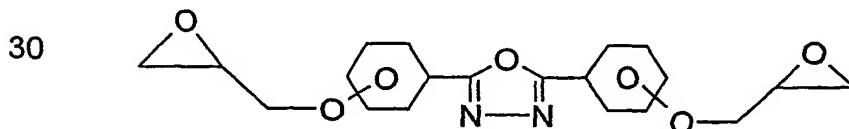
In EP 889 350 A1 examples are described with alkoxy substituted poly(phenyleneethynylene)s (PPEs) in ultra high molecular weight polyethylene as photoluminescent polymers.

Another type of display uses polarized electroluminescence as background illumination of LCDs. Luessem et al. (Liquid Crystal 21 (1996), 903) report the fabrication of polymer based LEDs showing polarized electroluminescence. The orientation of the molecules within the light emitting layer was accomplished by the self organization of liquid crystal polymers (LCPs) deposited onto a rubbed polyimide film serving as an alignment layer. A main chain polymer of the following structure was used as LCP with a maximum of emission at 450 nm



Furthermore bis((aryl)vinyl)benzenes, which may also comprise epoxy- or glycidyl-groups, are subject of the US 4,529,556. These compounds are said to be useful as dyes, ultraviolet light sensitizers and fluorescing agents.

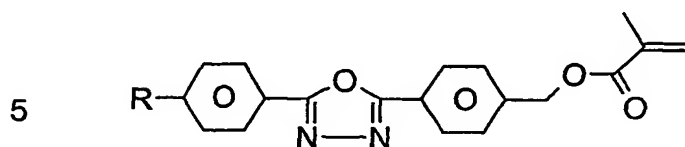
Korotkikh et al. (Chemistry Heterocyclic Compounds, 35, 1999, 358-362) propose luminescent epoxide polymers, suitable for polymeric casting and coatings that luminesce intensely upon UV radiation. Glycidyl ethers of 4,4'- and 3,3'-dihydroxy-2,5-diphenyloxadiazoles of the following formula were prepared



The preparation of charge transport polymers and copolymers for light emitting diodes with chemically bound oxadiazoles and such devices were

- 4 -

reported by Li et al., Adv. Mater. 7, 1995, 898-900. Methacrylate monomers of the following formula were synthesized



wherein R denotes phenyl or tert.-butyl.

10 The photoluminescence stability of a cyanoterphenyl chromophor in a liquid crystalline polymeric system was studied by Alcalá et al. (J. Appl. Phys. 88 (2000) 7124-7128 and 87 (2000) 274-279). It was found that the order parameter and consequently the anisotropy of emission is higher in polymers with a low crosslinking degree. The photoluminescent materials
15 were prepared by photopolymerization of a monoacrylate (NAP), a diacrylate (C6M), a cyanoterphenyl chromophor with an acrylate group (CNT), a photoinitiator and a thermal inhibitor. The orientation was achieved by introducing the monomer mixture into a planar cell with rubbed surfaces prior to polymerization. The monomers NAP and C6M
20 consisted of rod-like liquid crystalline or mesogenic groups where at one or both ends the polymerizable acrylate group was bound via a hexylene spacer group. In the resulting polymer the rodlike cyanoterphenyl chromophor group holds the same orientation as the LC or mesogenic groups being connected to the acrylate-built main chains.

25 A method of measuring the extent of cure of a polymerizing material, especially of a methacrylate or methacrylic bone cement, is described in the US 5,598,005. The change in peak fluorescence wavelength of a fluorophore is measured. 4-(N-methacryloyloxymethyl-N-methylamino)-4'-nitrostilbene is mentioned as an example of a fluorophor.
30

The monitoring of photoinitiated polymerization of methyl methacrylate (MMA) using reactive fluorescent probes was studied by Jager et al., Macromolecules 32, 1999, 8791-8799. 4-[N-(2-Methacryloyloxyethyl)-N-
35

- 5 -

methylamino]-4'-nitrostilbene among other fluorophores was investigated as a fluorescent probe.

5 Pollack et al. (Polym. Prepr., 41, 2000, 1140) studied the development of fluorescence-based fiber optic sensors for determining the degree of cure in thermosetting resins. N-methyl-N-[6-oxiranylmethoxy]hexyl]-4-[2-(4-nitrophenyl) ethenyl]-benzeneamine is mentioned as a fluorophor.

10 Chiral liquid crystalline polymer materials comprising at least one chemically bound chromophor group are a major component of pigment flakes disclosed in WO 98/42799. These pigment flakes are obtainable from a polymerizable mesogenic compound of the formula I*



15 wherein

P is a polymerizable group,

20 Sp is a spacer group,

X denotes -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -SO₂-O-,
-O-SO₂- or a single bond,

25 R is H or an alkyl radical in which H-atoms and/or CH₂-groups may be substituted and

CG is a chromophoric or fluorescent chromophoric group.

30 Beside several other chromophoric groups oxazole derivatives, e.g. 2,5-diphenyloxazole (PPO), benzoxazoles, like PBBO and POPOP, and polyphenylene derivatives are disclosed.

35 One of the aims of the present invention is to provide polymerizable, luminescent compounds, which are especially suitable for the manufacture

of luminescent polymer materials showing advantageous absorption and emission properties.

5 A further aim of this invention is to make available polymerizable, luminescent compounds, which are especially suitable for the production of anisotropic luminescent polymer materials showing advantageous anisotropic optical characteristics.

10 Another aim of the invention is to provide polymerizable mixtures for the production of luminescent and anisotropic luminescent polymer materials with the above mentioned characteristics.

15 Furthermore it is an aim of the present invention to make available luminescent as well as anisotropic luminescent polymer materials with the above mentioned characteristics.

Further aims of the invention are to extend the pool of polymerizable, luminescent compounds, of polymerizable mixtures comprising such compounds and of luminescent polymer materials available to the expert.

20 The aim of this invention is also to show advantageous uses of these polymerizable, luminescent compounds, mixtures and polymer materials.

25 Further aims of the invention relate to light emitting devices and optical or electrooptical display elements in which the polymer materials according to the invention are applied advantageously.

Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

30

35

Definition of Terms

5 The term luminescence means emission of electromagnetic radiation, preferably in, but not limited to, the visible spectrum, due to any kind of excitation, preferably by electromagnetic radiation (photoluminescence) or by an applied electric voltage (electroluminescence). The more general term luminescence encompasses phosphorescence and fluorescence, the latter being the preferred meaning.

10 The terms polymerizable or reactive mesogen, polymerizable or reactive mesogenic compound, polymerizable or reactive liquid crystal and polymerizable or reactive liquid crystalline compound as used in the foregoing and the following comprise compounds with a rodlike, boardlike or disk-like mesogenic group. These mesogenic compounds do not
15 necessarily have to exhibit mesophase behaviour by themselves. In a preferred embodiment of the present invention they show mesophase behaviour in mixtures with other compounds or after polymerization of the pure mesogenic compounds or of the mixtures comprising the mesogenic
20 compounds.

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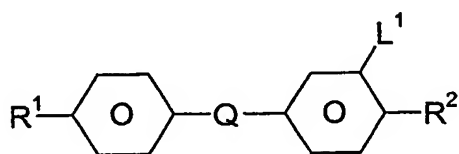
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Summary of the Invention

One of the objects of the present invention are polymerizable, luminescent compounds of formula I



10 wherein

R^1, R^2 are independently of each other H, halogen, NO_2 , CN, NCS, straight chain, branched or cyclic alkyl with 1 to 25 C-atoms wherein one or more CH_2 groups may also be replaced by $-\text{CO}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NR}^\circ-$, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$ in such a manner that O- and/or S-atoms are not linked directly to one another, and wherein one or more H-atoms may also be replaced by F or Cl, or denotes $\text{P}-(\text{Sp}-\text{X})_n-$,

15

20 Sp is a spacer group with 1 to 20 C-atoms,

P is a polymerizable group,

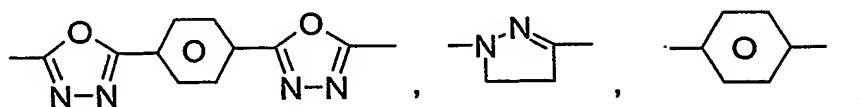
X is $-\text{O}-$, $-\text{S}-$, $-\text{CO}-$, $-\text{COO}-$, $-\text{OCO}-$, $-\text{CO}-\text{NR}^\circ-$, $-\text{NR}^\circ-\text{CO}-$, $-\text{NR}^\circ-$ or a single bond,

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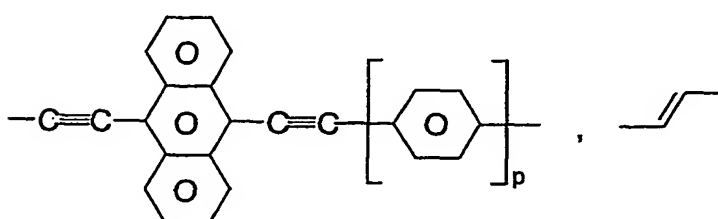
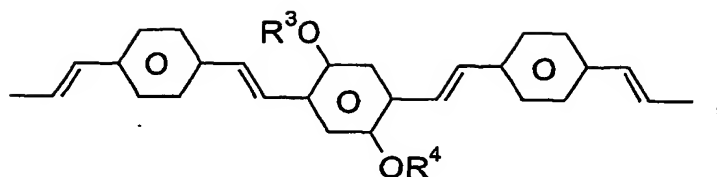
n is 0 or 1,

R° is H or alkyl with 1 to 5 C-atoms,

30 Q is one of the following subformulae



- 9 -




R^3, R^4 are independently of each other straight chain, branched or cyclic alkyl with 1 to 15 C-atoms wherein one or more H-atoms may also be replaced by F or Cl, or denotes $P-(Sp-X)_n-$,

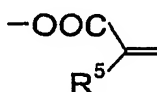
p is 0 or 1,

L^1 is H, F or CN


with the proviso that

a) the compounds of formula I contain one, two or more groups $-(X-Sp)_n-P$,

b) if Q denotes , then R^1 is $-O-Sp-P$,

R^2 is $-CN$, wherein P is not 

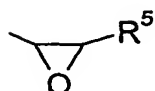
with R^5 denoting H, Cl or alkyl with 1 to 5 C-atoms,

c) if Q denotes , then R^1 is $-N \begin{smallmatrix} \nearrow Sp-P \\ \searrow R^3 \end{smallmatrix}$ and

R^2 is $-NO_2$

- 10 -

i) wherein P is not $\text{---OOC} \begin{array}{c} \diagup \\ \text{R}^5 \end{array} \text{=}$ and P is not



or

ii) L¹ is F or CN.

Another object of the invention are polymerizable mixtures comprising at least one polymerizable, luminescent compound according to this invention.

A further object of this invention are luminescent polymer materials obtainable by polymerizing a polymerizable compound or mixture according to the invention.

Another object of the invention is the use of a polymerizable, luminescent compound or of a polymerizable mixture, both according to the invention, for the manufacture of photoluminescent and/or electroluminescent polymer materials.

An additional object of the invention is the use of a luminescent polymer material according to the invention as a photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element.

Another object of the invention are light emitting devices comprising a polymer material according to the invention as a photo- and/or electroluminescent material.

A further object of the invention are optical or electrooptical display elements comprising a luminescent polymer material according to the invention as a photo- and/or electroluminescent material.

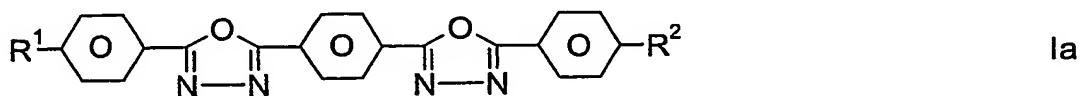
Detailed Description of the Invention

In the following the groups, substituents and indices R^0 , R^1 , R^2 , R^3 , R^4 , Q, Sp, P, X, L^1 , n and p have the above given meaning unless stated otherwise.

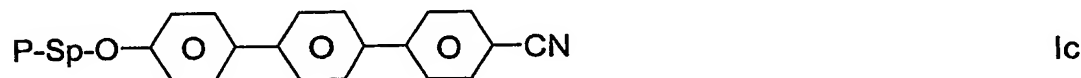
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Preferred compounds of formula I are those of the following subformulae

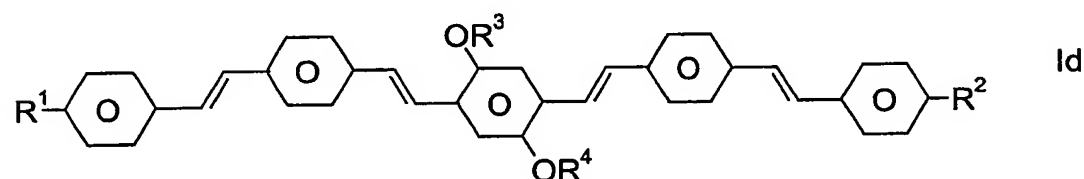
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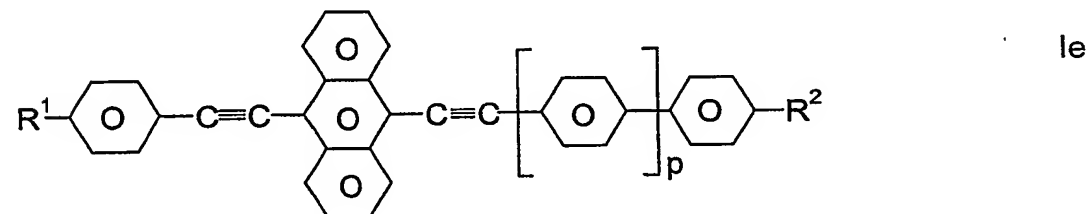
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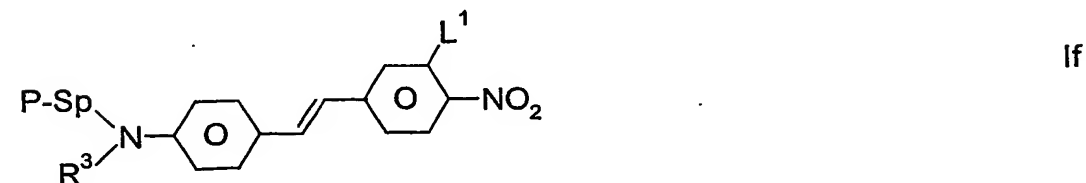
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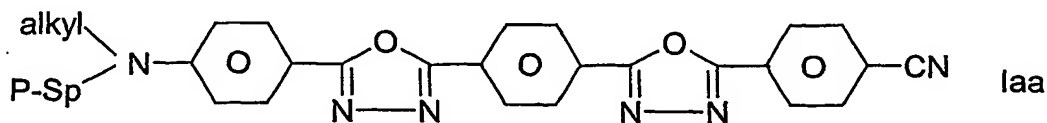
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The inventive polymerizable, luminescent compounds of formula I have the major advantage that they can be chemically bound to the polymer matrix.

Unlike those luminescent compounds which are not polymerizable and therefore not chemically bound, no diffusion processes may alter their absorption and emission properties. Furthermore the orientation of the compounds according to the invention may be frozen by a polymerization and/or cross-linking step, leading to materials with anisotropic absorption and emission characteristics which are stable over time. Further advantages of the inventive compounds, especially those of formulae Ia to If, are:

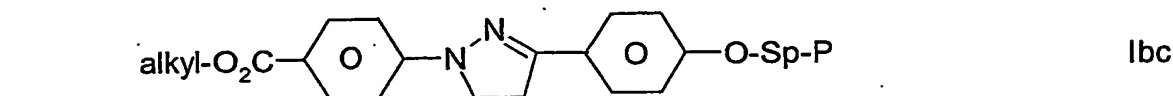
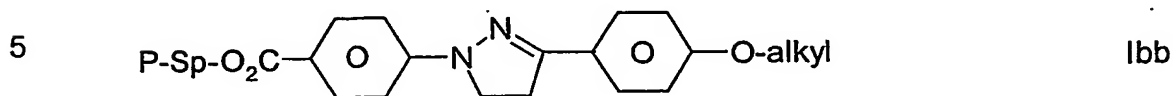
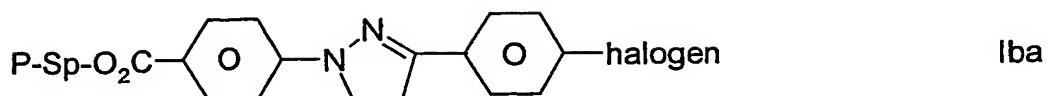
- they exhibit advantageous absorption and emission characteristics,
- they show a high fluorescence quantum yield,
- the luminescence of these compounds exhibits a small band width of the emission wavelength,
- they show advantageous excitation wavelenghts, especially in the region $390 \text{ nm} \leq \lambda \leq 450 \text{ nm}$,
- they have a high stability under excitation with UV-light, especially at wavelengths $\lambda \geq 390 \text{ nm}$,
- they show a high ordering tendency in polymerizable mixtures according to the invention yielding a high orientation degree,
- in an oriented state they show a high degree of optical anisotropy,
- the starting materials can be obtained commercially or synthesized economically using methods known from the literature,
- they exhibit a good solubility in polymerizable mixtures, especially in mixtures according to the invention.

Particularly preferred compounds of subformula Ia are those of the following subformula



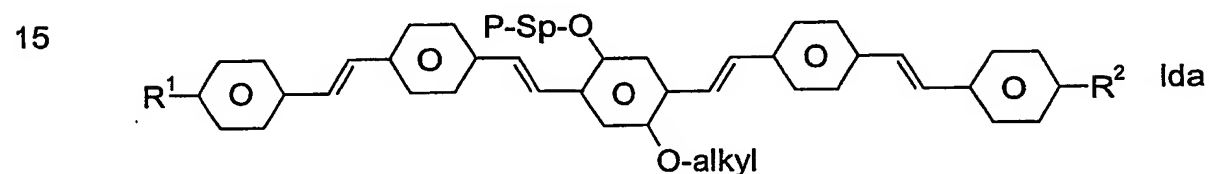
Particularly preferred compounds of subformula Ib are those of the following subformulae

- 13 -



10 wherein halogen denotes F, Cl or Br.

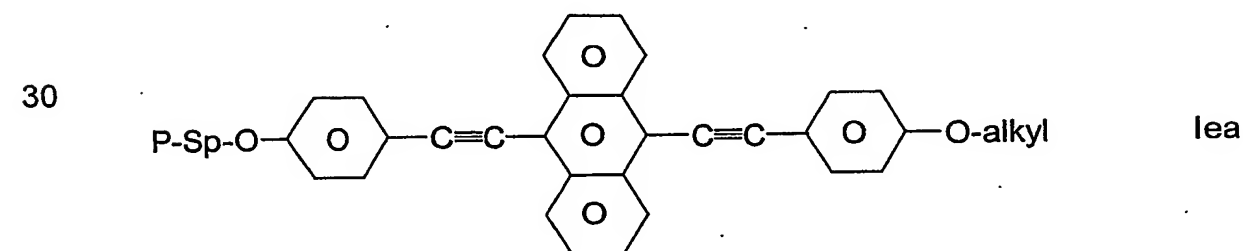
Particularly preferred compounds of formula Id are those of the formula Ida



20 wherein

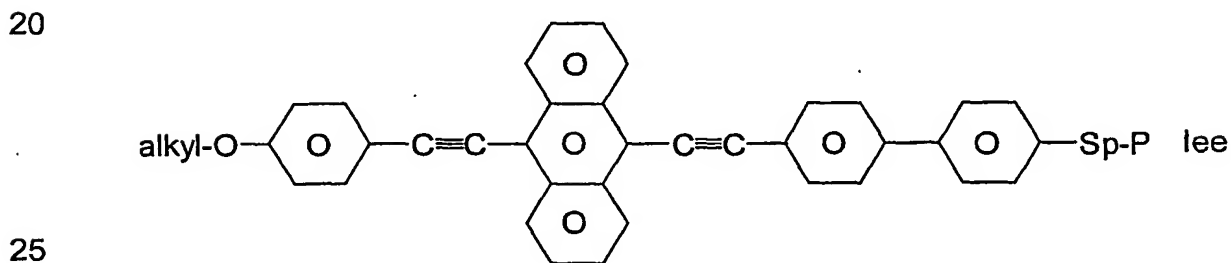
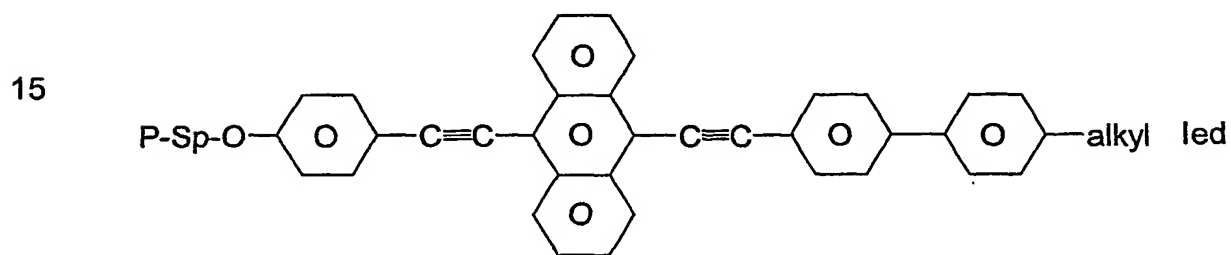
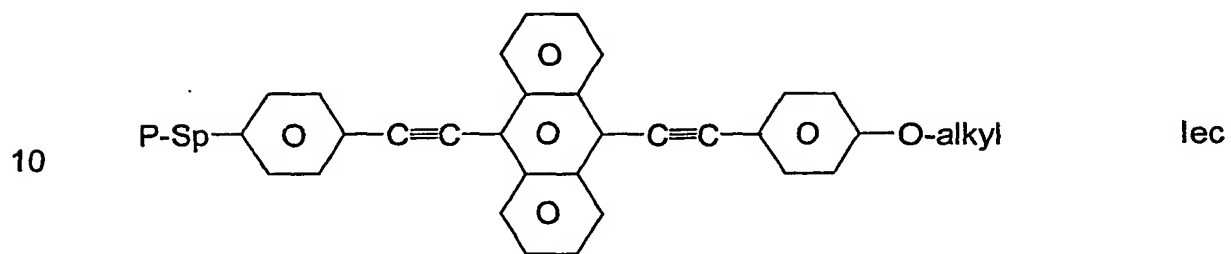
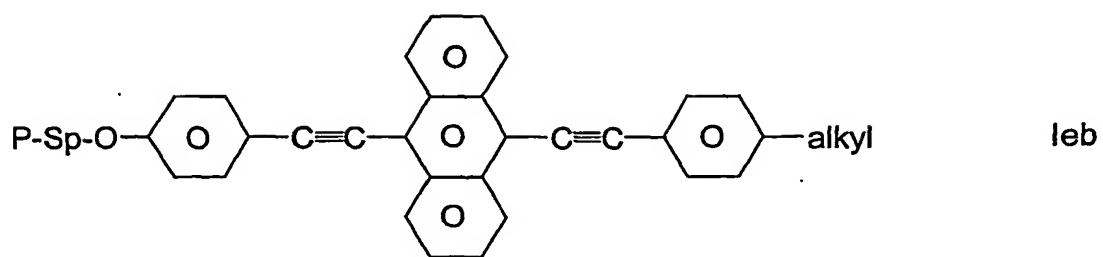
R¹, R² are defined as above, preferably denote independently of each other H or alkyl.

25 Particularly preferred compounds of formula Ie are those of the formulae Iea to Iee



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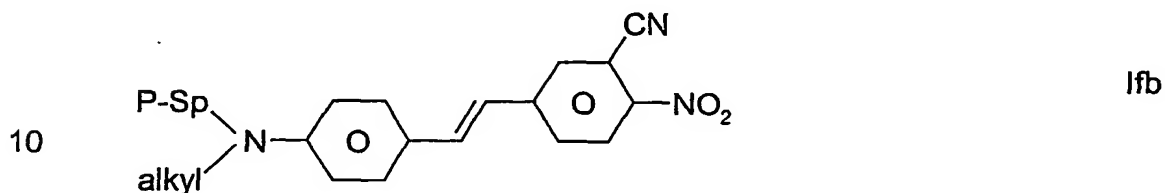
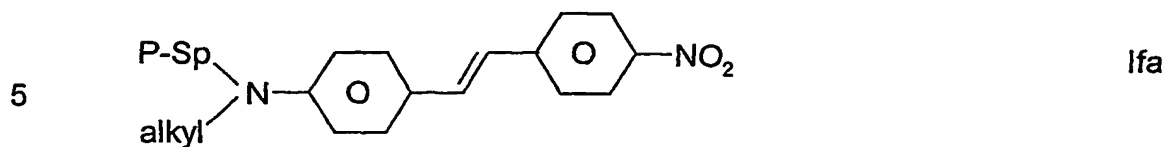


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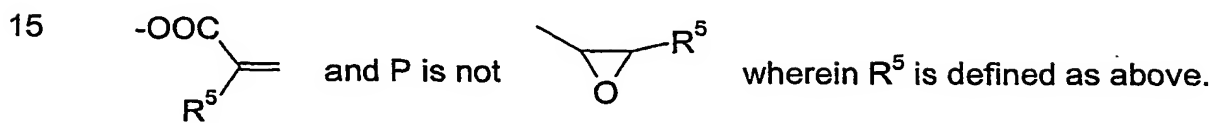
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Particularly preferred compounds of formula If are those of the formulae Ifa and Ifb



with the proviso that in formula Ifa P is not



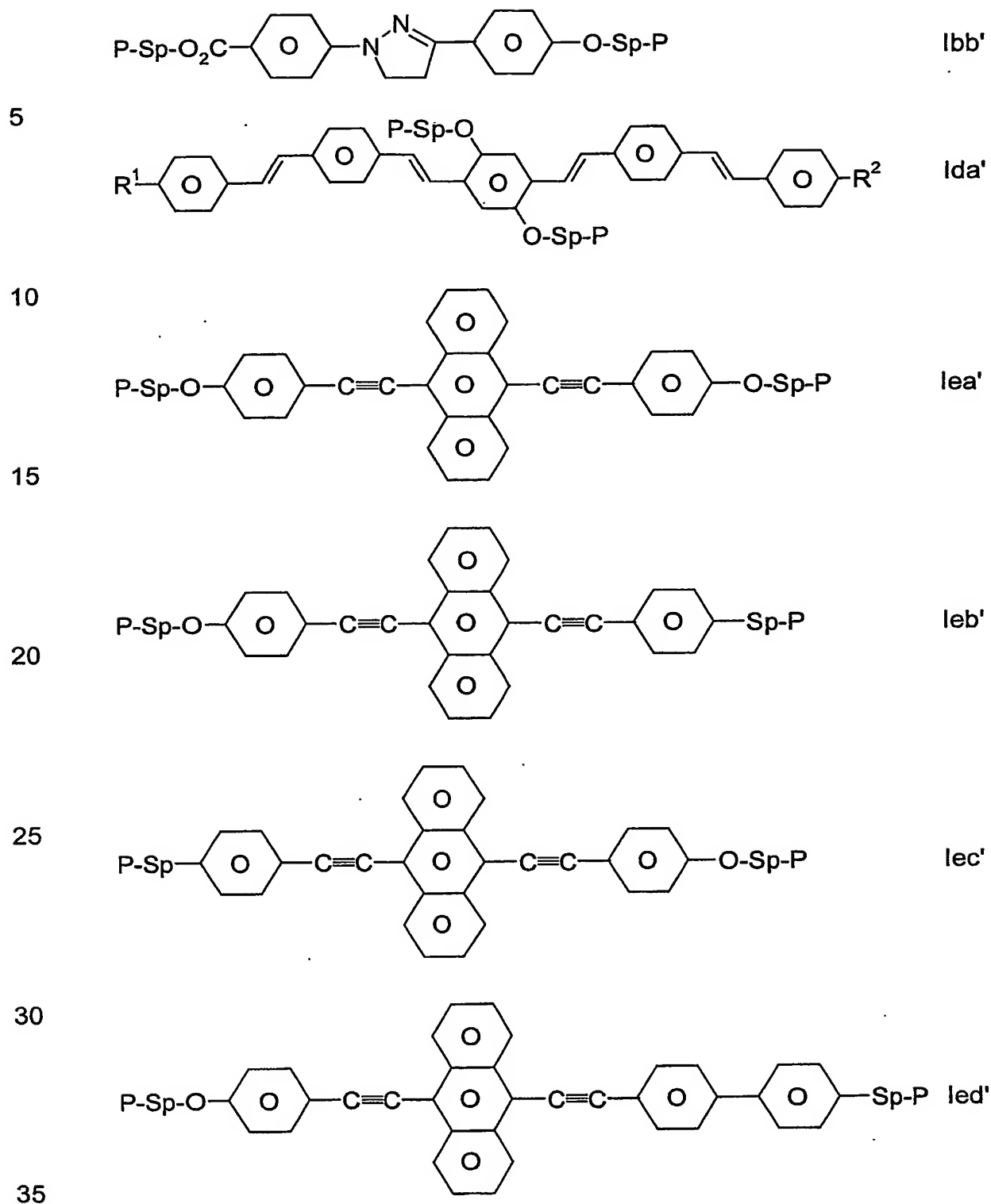
20 In the above and following formulae the term alkyl denotes a straight chain, branched or cyclic alkyl group with 1 to 12 C-atoms wherein one or more H-atoms can also be replaced by F or Cl.

25 The above mentioned compounds of formula I may contain one (monofunctional) or two or more (multifunctional) polymerizable groups -(X-Sp)_n-P. One or two polymerizable groups are preferred.

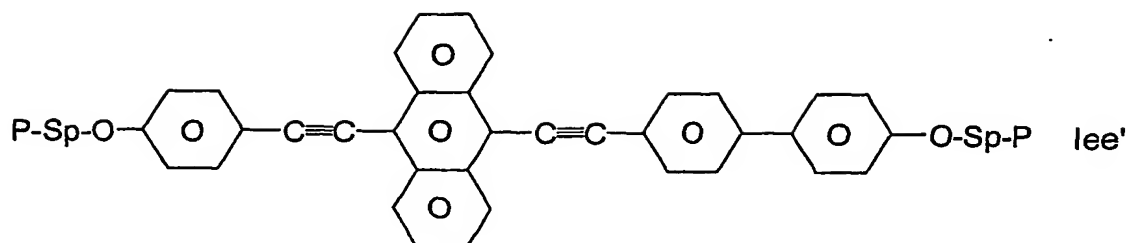
30 Preferred compounds with two polymerizable groups are of the formulae lbb, lbc, lda, lea to lee, wherein in each case one of the groups "-alkyl" is replaced by -Sp-P, wherein Sp and P have the same or different meanings compared to the existing group -Sp-P.

Especially preferred compounds with two polymerizable groups are selected from the following group of formulae

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The polymerizable mixture according to the invention comprises at least one polymerizable, luminescent inventive compound. Preferably it comprises one compound of formula I, but it may also comprise 2, 3 or more compounds of formula I. Preferably the mixture comprises further components as described below, but the mixture may also consist of 1, 2, 3 or more compounds of formula I only. Additionally the inventive mixture may contain other luminescent compounds, which may be polymerizable or not. Advantageously the luminescent compounds are selected according to their emission wavelengths in such a way that their combination yields the desired luminescent color.

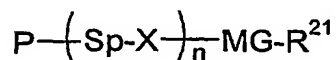
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Furthermore one or more first luminescent compounds may be combined with one or more second luminescent compounds such that the emission wavelengths of the first compounds lie within the absorption region, preferably the maximum absorption, of the latter compounds. Thus excitation at the absorption wavelength of the first compounds yields emitted light of the emission wavelengths of the second compounds.

Preferably the inventive mixture further comprises at least one polymerizable mesogenic compound of formula II

30



II

wherein

35

P is a polymerizable group,

Sp is a spacer group having 1 to 20 C-atoms,

X is a group selected from -O-, -S-, -CO-, -COO-, -OCO-,
-O-COO-, -SO₂-O-, -O-SO₂- or a single bond,

n is 0 or 1,

R²¹ is H or an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or alternatively R²¹ is halogen, cyano or has independently one of the meanings given for P-(Sp-X)_n,

MG is a mesogenic or mesogeneity supporting group.

The mixture according to this particularly preferred embodiment preferably comprises one to six, most preferably two to four different mesogens according to formula II having one or two, preferably one, polymerizable functional groups.

The mesogenic or mesogeneity supporting group MG in formula II is preferably selected of formula III:



wherein

$A^{31}, A^{32},$
 A^{33}

being independently from one another 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, 1,4-cyclohexenylene or naphthalene-2,6-diyl, it being possible for all these groups to be unsubstituted, mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl,

Z^{31}, Z^{32}

being independently from one another -O-, -CO-, -COO-, -OCO-, -O-SO₂-, -SO₂-O-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond and

m being 0, 1 or 2.

Bicyclic and tricyclic mesogenic groups are preferred.

Of the compounds of formula II especially preferred are those in which R²¹ is F, Cl, cyano, or optionally halogenated alkyl or alkoxy, or has the meaning given for P-(Sp-X)_n-, and MG is of formula III wherein Z³¹ and Z³² are -COO-, -OCO-, -CH₂-CH₂-, -CH=CH-COO-, -OCO-CH=CH- or a single bond.

A smaller group of preferred mesogenic groups MG of formula III is listed below. For reasons of simplicity, Phe in these groups is 1,4-phenylene, PheL is a 1,4-phenylene group which is substituted by at least one group L, with L being F, Cl, CN, NO₂ or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms, and Cyc is 1,4-cyclohexylene.

-Phe-Z ³² -Phe-	III-1
-Phe-Z ³² -Cyc-	III-2
-PheL-Z ³² -Phe-	III-3
-PheL-Z ³² -Cyc-	III-4

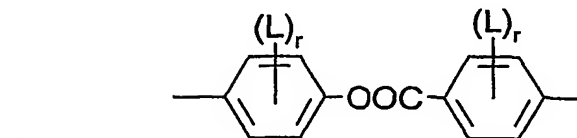
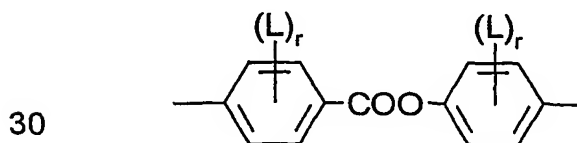
	-Phe-Z ³² -PheL-	III-5
	-Phe-Z ³¹ -Phe-Z ³² -Phe-	III-6
	-Phe-Z ³¹ -Phe-Z ³² -Cyc-	III-7
	-Phe-Z ³¹ -Phe-Z ³² -PheL-	III-8
	-Phe-Z ³¹ -PheL-Z ³² -PheL-	III-9
5	-Phe-Z ³¹ -Cyc-Z ³² -Phe-	III-10
	-Phe-Z ³¹ -Cyc-Z ³² -Cyc-	III-11
	-Phe-Z ³¹ -PheL-Z ³² -Phe-	III-12
	-PheL-Z ³¹ -Phe-Z ³² -Phe-	III-13
	-PheL-Z ³¹ -Phe-Z ³² -PheL-	III-14
10	-PheL-Z ³¹ -PheL-Z ³² -Phe-	III-15
	-PheL-Z ³¹ -PheL-Z ³² -PheL-	III-16

In these preferred groups Z³¹ and Z³² have the meaning given in formula III described above. Preferably Z³¹ and Z³² are -O-, -COO-, -OCO-, -CO-,
 15 -O-SO₂-, -SO₂-O-, -CH₂CH₂- or a single bond.

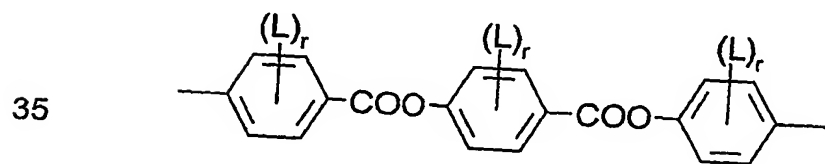
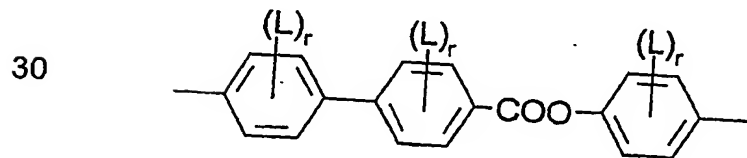
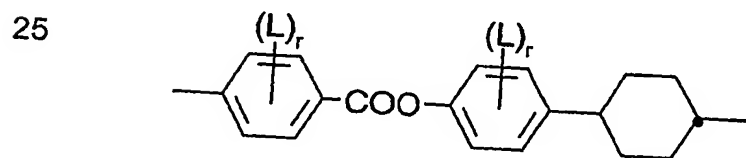
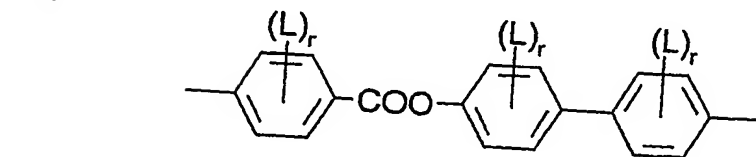
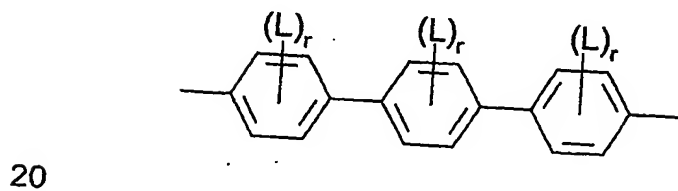
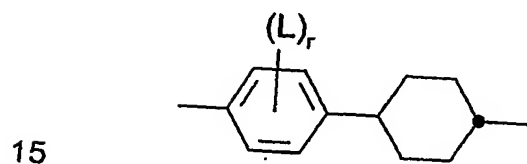
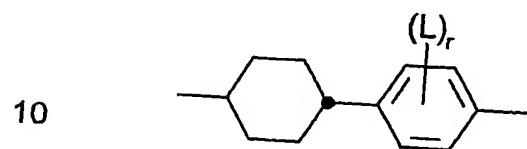
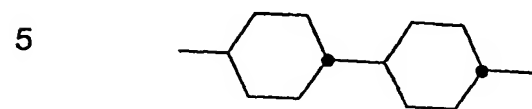
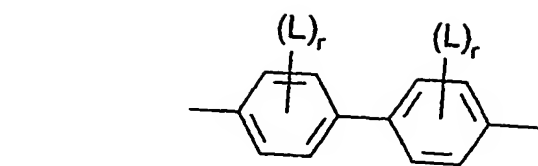
PheL in these preferred formulae is very preferably denoting 1,4-phenylene which is monosubstituted with L in the 2- or 3-position or disubstituted with L in the 2- and 3-position or in the 3- and 5-position, with
 20 L having each independently one of the meanings given above.

L is preferably F, Cl, CN, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, CF₃, OCF₃, OCHF₂, OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ and OCF₃, most preferably F, CH₃, OCH₃ and COCH₃.
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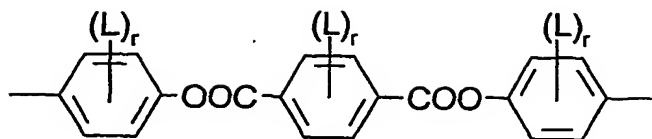
MG in formula III particularly preferably has one of the following meanings



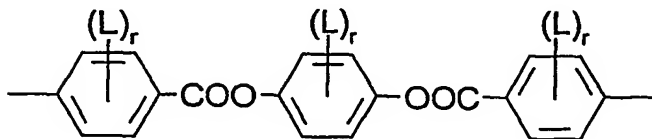
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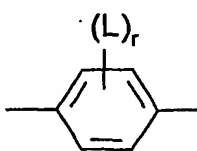
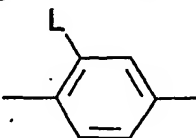
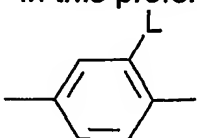
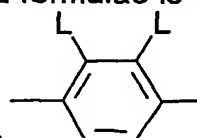
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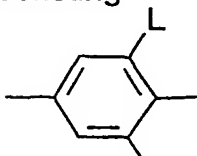
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wherein L has the meaning given above and r is 0, 1 or 2.

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The group  in this preferred formulae is very preferably denoting ,  or , furthermore

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, with L having each independently one of the meanings given above, preferably -F.

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R^{21} in these preferred compounds is particularly preferably CN, F, Cl, OCF_3 , or an alkyl or alkoxy group with 1 to 12 C atoms or has one of the meanings given for $P-(Sp-X)_n$.

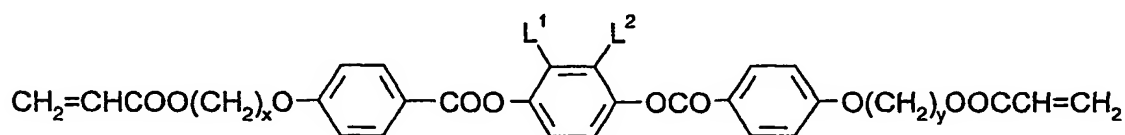
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Typical examples representing polymerizable mesogenic compounds of the formula II can be found in WO 93/22397; EP 0 261 712; DE 195 04 224; DE 44 08 171 and DE 44 05 316. The compounds disclosed in these documents, however are to be regarded merely as examples that should not limit the scope of this invention.

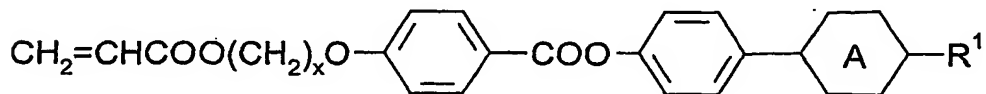
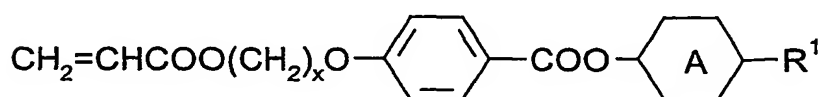
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Furthermore, typical examples representing polymerizable mesogenic compounds like those of formula II are shown in the following list of compounds, which is, however, to be understood only as illustrative without limiting the scope of the present invention:

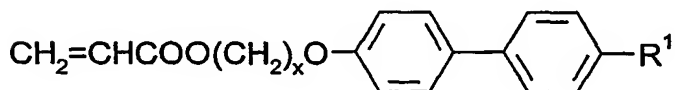
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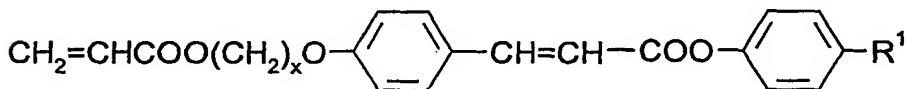
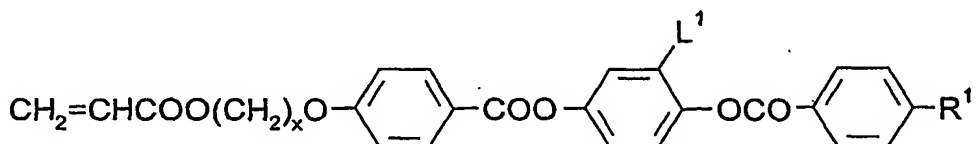
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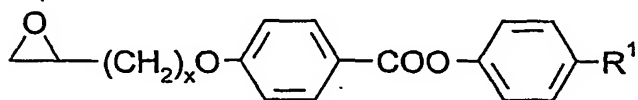
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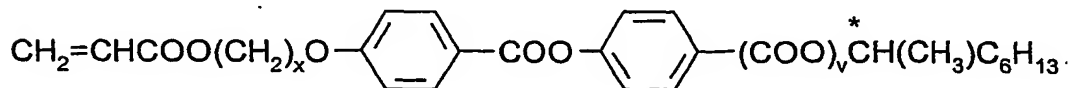
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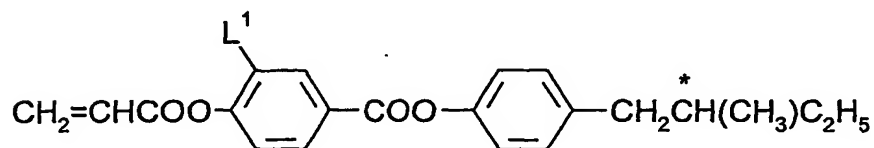
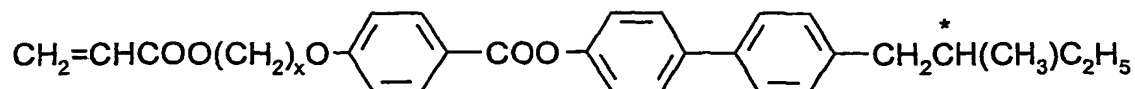


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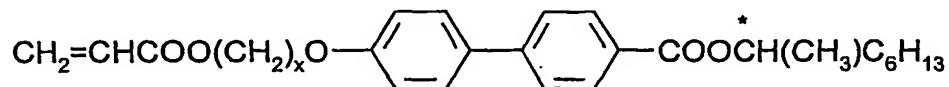


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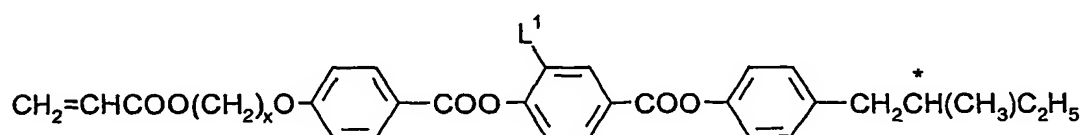
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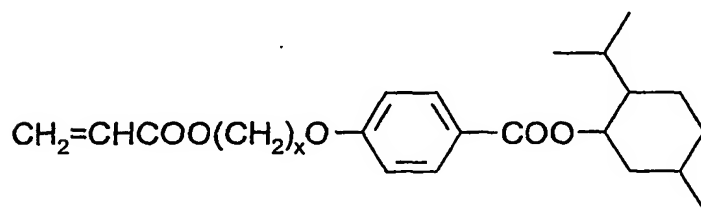
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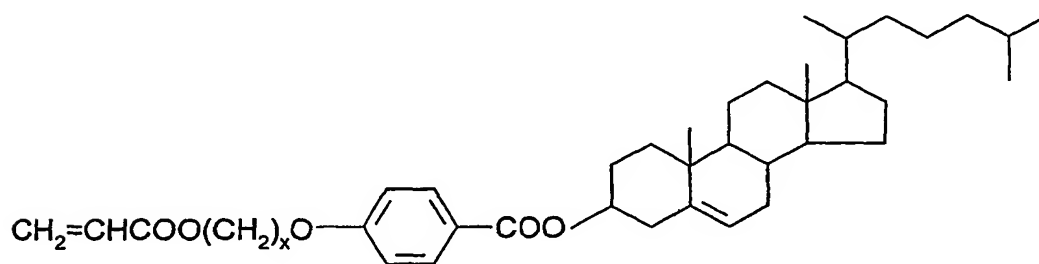
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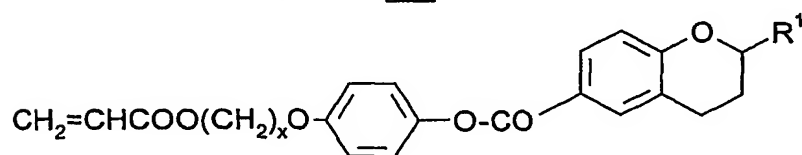
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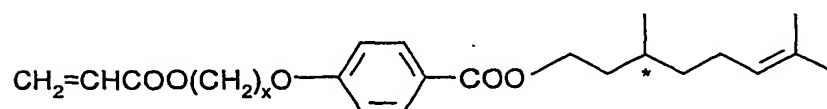
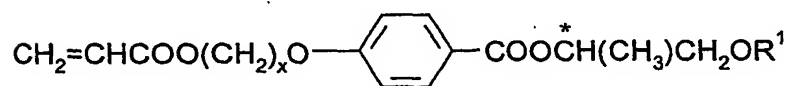
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In these compounds x and y are each independently 1 to 12, v is 0 or 1, A is a 1,4-phenylene or 1,4-cyclohexylene group, R¹ is halogen, cyano or an optionally halogenated alkyl or alkoxy group with 1 to 12 C atoms and L¹ and L² are each independently H, F, Cl, CN or an optionally halogenated alkyl, alkoxy or alkanoyl group with 1 to 7 C atoms.

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In a preferred embodiment the polymerizable mixture according to the invention further comprises at least one polymerizable and photoorientable compound. Photoorientable compounds are uniformly orientable by exposure to polarized electromagnetic radiation, especially linearly polarized light. Their orientation induces a co-operative alignment of the side groups and co-components to the same direction and a comparable degree of order. One known process is the photo-induced isomerization, e.g. of azo-groups, cinnamic acid ester groups or cinnamic acid amid groups. Known photoorientable compounds and techniques are described e.g. by M. Schadt (Information Display 12, 1997, 14-18; Journal of the SID 5/4, 1997, 367-370 and literature cited therein) and in WO 00/34808. The orientation of these polymerizable and photoorientable compounds and of the other components of the polymerizable mixture is frozen by a subsequent polymerization and/or cross-linking, which is preferably induced by electromagnetic radiation and may be done simultaneously with the photoorientation process. An annealing of the thus photo-oriented, polymerized and/or cross-linked mixture, preferably above the glass transition temperature, can result in a significant amplification of the photo-induced anisotropy.

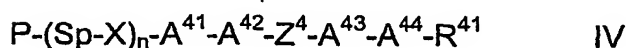
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Preferred compounds which are polymerizable and photoorientable are denoted by the formula IV



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wherein

P, Sp, X and n are defined as above,

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R⁴¹ has one of the meanings given for R¹,

$A^{41}, A^{42},$
 A^{43}, A^{44}

are independently of each other 1,4-phenylene, wherein 1, 2, 3 or 4 H-atoms may be replaced by F or Cl,

5 A^{41}, A^{44}

may in addition to the above given meaning denote independently of each other a single bond,

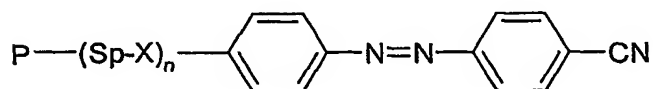
Z^4

is $-N=N-$, $-CH=CH-$ or $-(O)_{s1}-(CH_2)_{s2}-O-CO-CH=CH-$ with $s1$ being 0 or 1 and $s2$ being 0 to 6.

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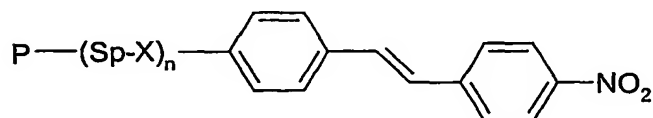
Especially preferred compounds of formula IV are selected from the following list of formulae

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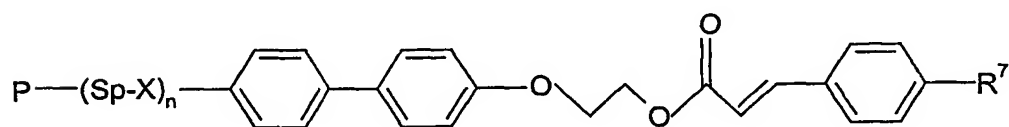
IVa

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IVb

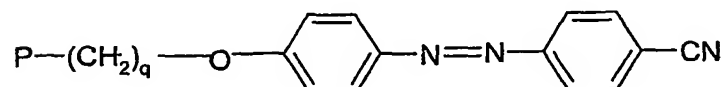
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IVc

wherein R^7 is $-O\text{-alkyl}$, $-N\begin{smallmatrix} H \\ \text{alkyl} \end{smallmatrix}$ or $-N\begin{smallmatrix} \text{alkyl} \\ \text{alkyl} \end{smallmatrix}$

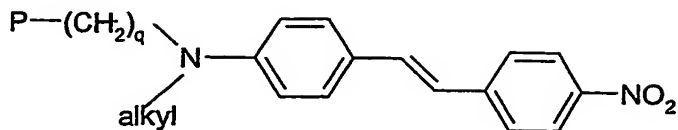
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IVd

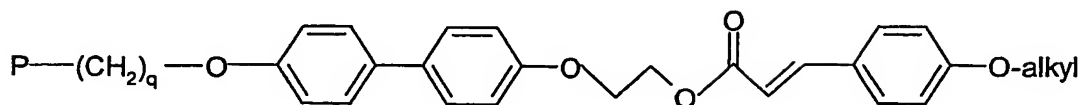
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IVe

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IVf

wherein q is 1 to 12.

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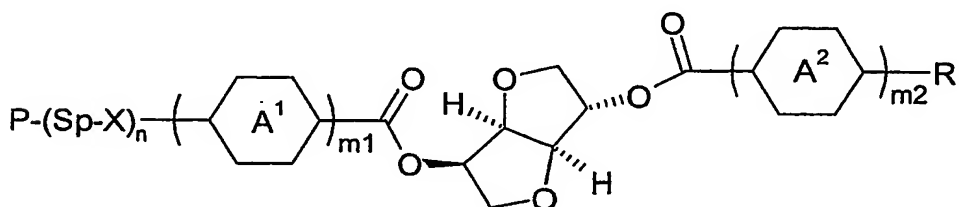
The polymerizable mixture according to the invention preferably contains at least one photoinitiator, if the polymerization step is to be induced by actinic radiation, especially light in the UV or visible range.

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Furthermore if a cross-linked polymer material is desired, the inventive polymerizable mixture may also comprise a non-mesogenic compound having two or more polymerizable functional groups.

The polymerizable mixture according to the invention may additionally contain one or more chiral compounds which comprise a group having at least one center of chirality. Especially suitable are those chiral compounds described in WO 98/42799, especially those of the formula I, wherein MG-R is selected according to formula IIa and IIb as disclosed in WO 98/42799 which is incorporated herein by reference. Particularly preferred compounds are selected of the following formula

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wherein the rings A^1 , A^2 are independently of each other 1,4-phenylene or 1,4-cyclohexylene, m_1 , m_2 are independently of each other 1 or 2 and R has one of the meanings of R^1 or denotes $-(X-Sp)_n-P$. Groups, e.g. A^1 , A^2 , X, Sp, P, occurring twice may have identical or different meanings.

35

Furthermore the polymerizable mixture may additionally contain one or more compounds having electron- and/or hole-transport properties. The addition of such compounds is especially useful in the preparation of electroluminescent polymer materials and devices. Besides the function as an emitter, the electroluminescent layer of such devices, e.g. OLEDs or backlights, may also have the function as an electron- and/or hole-transport layer. These electron- and/or hole-transport compounds may be polymerizable or non-polymerizable.

Compounds with electron-transport capabilities are listed below, but are not limited to these examples:

2-(4-(1-Methyl-ethyl)-phenyl)-6-phenyl-4H-thiopyran-4-ylidene-propanedinitril-1,1-dioxide

1,3-Bis(4-(4-diphenylamino)-phenyl-1,3,4-oxadiazol-2-yl)benzene

2-(4-Biphenyl)-5-(4-tertbutylphenyl)-1,2,3-oxadiazole

2-(4-Methylphenyl)-6-phenyl-4H-thiopyran-4-ylidene]-propanedinitril-1,1-dioxide

Compounds with hole-transport capabilities are listed below, but are not limited to these examples:

4,4',4''-Tris(carbazol-9-yl)-triphenylamine

1,3-Bis(4-(4-diphenylamino)-phenyl-1,3,4-oxadiazol-2-yl)benzene

1,1-Bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane

N,N,N',N'-Tetrakis(4-methylphenyl)-benzidine

N,N,N',N'-Tetrakis(3-methylphenyl)-benzidine

4,4'-Bis(dibenz-azepin-1-yl)-biphenyl

N,N'-Bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine

- 29 -

N,N,N',N'-Tetraphenylbenzidine

N,N'-Bis-(4-methylphenyl)-N,N'-bis-(phenyl)-benzidine

4,4'-Bis(carbazol-9-yl)-biphenyl

N,N'-Di-(4-methyl-phenyl)-N,N'-diphenyl-1,4-phenyldiamine

4-(2,2-Bisphenyl-ethen-1-yl)-triphenylamine

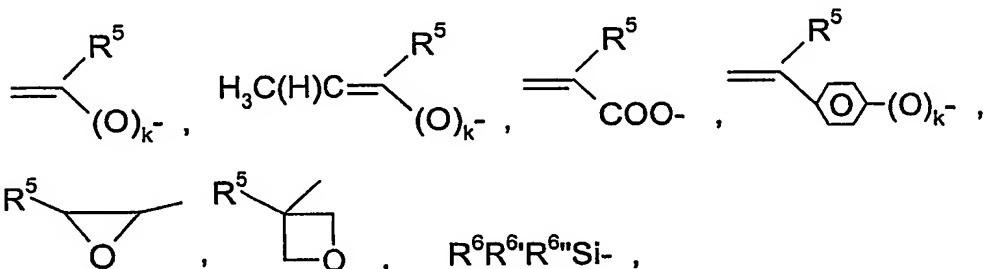
N-(Biphenyl-4-yl)-N,N-bis(3,4-dimethyl-phenyl)-amine

N-Biphenylyl-N-phenyl-N-(3-methylphenyl)-amine

4,4',4''-Trismethyl-triphenylamine

In the following, preferred meanings of groups and substituents are described.

P is preferably selected from the following groups



wherein

R^5 is H, Cl or alkyl with 1 to 5 C-atoms, preferably methyl, ethyl or n-propyl,

R^6 , $R^{6'}$, $R^{6''}$ are independently of each other -Cl, -O-alkyl and/or -O-CO-alkyl with alkyl having 1 to 5 C-atoms and

k is 0 or 1.

P is particularly preferably a vinyl group, an acrylate group, a methacrylate group, a propenyl ether group or an epoxy group, very particularly preferably an acrylate or methacrylate group.

A preferred meaning of R^1 , R^2 , R^{21} and/or R^{41} is alkyl, alkoxy and oxaalkyl.

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An alkyl-radical may be straight-chain, branched or cyclic. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl or pentadecyl, for example.

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An alkoxy-radical, i.e. where the terminal CH_2 group is replaced by $-O-$, may be straight-chain, branched or cyclic. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy or octoxy, furthermore methoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

15

A preferred oxaalkyl-radical, i.e. where one CH_2 group is replaced by $-O-$, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

25

In the compounds of formula I, II and IV R^1 , R^2 , R^{21} and/or R^{41} may be an achiral or a chiral group.

Preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleryloxy, 4-

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methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, for example.

5

In addition, mesogenic compounds of the formula I, II and IV containing an achiral branched group R^1 , R^2 , R^{21} and/or R^{41} can be of importance as comonomers, for example, as they reduce the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropoxy and 3-methylbutoxy.

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As for the spacer group Sp in formula I, II and IV all groups can be used that are known for this purpose to the skilled in the art. The spacer group Sp is preferably linked to the polymerizable group P by an ester or ether group or a single bond. The spacer group Sp is preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH_2 groups may be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -CO-O-, -O-CO-O-, -SO₂-O-, -O-SO₂-, -CH(halogen)-, -CH(CN)-, -CH=CH- or -C≡C-.

25

Typical spacer groups Sp are for example $-(CH_2)_o-$, $-(CH_2CH_2O)_r-$, $-CH_2CH_2-$, $-CH_2CH_2-S-CH_2CH_2-$ or $-CH_2CH_2-NH-CH_2CH_2-$, with o being an integer from 2 to 12 and r being an integer from 1 to 3.

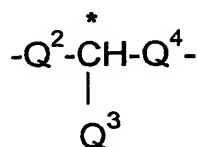
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Preferred spacer groups Sp are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene and 1-methylalkylene, for example.

35

In one embodiment of the invention the polymerizable compounds of formula I, II and/or IV comprise a spacer group Sp that is a chiral group of the formula V:

- 32 -



V

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wherein

Q² is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

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Q³ is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms,

Q⁴ is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q².

15

In particular preferred are compounds of formula I, II and IV wherein n is 1.

In the event that the compounds of formula I, II and/or IV contain a group, like P-Sp-X- or alkyl, twice or more times these groups may be identical or different.

20

The polymerizable compounds of formula I and II as disclosed in the foregoing and the following can be prepared by methods which are known per se and which are described in the documents cited above and, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Further methods of preparation can be taken from the examples.

25

The luminescent polymer material according to the invention is obtainable by polymerizing an inventive polymerizable mixture.

30

Two different types of luminescent polymer materials may be distinguished. In the first kind of luminescent polymer materials the luminescent chromophor units, also denoted as lumophor units or

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fluorophor units in the case of fluorescence, are just contained in a polymer matrix serving as a host, with no chemical bonds formed between the lumophor units and the polymer chains. The second kind of luminescent polymer materials shows lumophor units being chemically bound to the polymer chains. Here the lumophor units are part of the main chains and/or the side chains. Luminescent polymer materials according to this invention are preferably such of the second kind. In addition to the lumophor unit or units being part of the main chain and/or the side chains, it is possible that further lumophor units are just contained in the polymer matrix without any chemical bonds to the polymer chains.

Preferably such a material is obtainable by a process comprising the following steps:

- a) forming a thin layer of the polymerizable mixture,
- b) aligning the molecules of the compounds of the mixture in the thin layer into a uniform orientation or a patterned orientation such that in each pattern the orientation is uniform,
- c) polymerizing said polymerizable material.

Especially suitable for this process are polymerizable mixtures comprising at least one polymerizable mesogenic compound according to the invention.

Preferably the step a) is performed by coating a thin layer of the polymerizable mixture onto a carrier material or onto a substrate or between two substrates. The thin film has preferably a thickness in the range of 1 μm to 5 mm, especially 1 μm to 1 mm, most preferably in the range of 2 μm to 500 μm . If one or two substrates are used, after the polymerizing step c) one or both substrates are removed preferably. Advantageously the carrier material and/or the substrate are transparent, at least in the wavelength range of the excitation and/or emission of the luminescent polymer material. By this procedure a luminescent polymer film of the above thickness is obtained, which may be structured or

unstructured. The structuring may be achieved by applying the luminescent polymer material on a patterned substrate or the material or the film is patterned by known techniques like lithography.

5 The orientation is achieved by known orientation techniques, like those mentioned in the introduction. A preferred technique is the photo-orientation, e.g. described by M. Schadt as cited above. If a photo-orientation step is applied, those polymerizable mixtures are preferred comprising at least one polymerizable and photoorientable compound according to the invention. Also the technique described in WO 00/34808
10 to manufacture layers of cholesterically ordered polymer material is applicable.

The polymerizing step c) is preferably done by exposure of the oriented thin layer to heat or to actinic radiation.

15 The polymer chains may be in part or totally cross-linked. In the curing process the polymerizable groups of the aligned material react to form a crosslinked polymer film. Thereby the orientation is frozen in. The polymerization can be carried out for example by exposure to UV light with
20 the help of a photoinitiator that decomposes under irradiation to produce free radicals that start the polymerization reaction. In another preferred embodiment a cationic photoinitiator is used that photocures with cations instead of free radicals. The polymerization may also be started by an initiator that decomposes when heated above a certain temperature.

25 To exclude oxygen that may inhibit the free radical polymerization, a layer, e.g. comprising PET, may be laminated on top of the thin layer, or alternatively the curing can be carried out under a nitrogen atmosphere. When using a cationic photoinitiator oxygen exclusion is not needed, but
30 water should be excluded.

As described above, it may be advantageous to anneal the polymer material, especially above the glass transition temperature of the material, in order to amplify the anisotropy and thus to yield a higher dichroitic ratio.

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The annealing is preferably performed between one hour and several days, especially 2 hours up to 3 days.

5 These methods, however are only to be understood as examples that should not limit the scope of the invention. The person skilled in the art can easily find other suitable ways to carry out the polymerization.

10 Since the mixture may contain both polymerizable components with one (monofunctional) and with two or more polymerizable groups (multifunctional), polymerization and crosslinking are carried out in the same process.

15 By varying the concentration of the multifunctional mesogenic or non mesogenic components the crosslink density and thereby the product properties, such as the glass transition temperature, the temperature dependence of the optical properties, the thermal and mechanical stability and the solvent resistance can be tuned easily.

20 The luminescent polymer material according to the invention may be used for the manufacture of pigment flakes. The obtained luminescent polymer film is grinded into small particles of the desired dimensions to obtain luminescent pigment flakes. If according to step a) a carrier material is coated, preferably a platelet shaped carrier material is chosen. As carrier material for example natural or synthetic mica (muscovite or phlogopite), kaoline, talc, silica flakes, glass flakes or mixtures of two or more of these materials can be used. In a preferred embodiment of the present invention mica is used as carrier material. A detailed description of the manufacture of pigment flakes, their characteristics and their use is given in the WO 98/42799 which is incorporated by reference. One or more compounds of formula I according to this invention may be used instead of or in addition to compounds of formula I*, as described in WO 98/42799 and in the prior art section of this application.

35 The luminescent polymers according to the invention and products made thereof may be used in display devices mentioned in the introduction. Furthermore they may be used in an electrooptic color display e. g.

according to US 4,822,144 or WO 00/57239, where a backlight, switching elements and a luminescent pattern are combined.

5 The complete disclosure of all applications, patents and publications mentioned hereinbefore and hereinafter is introduced into this application by way of reference.

10 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

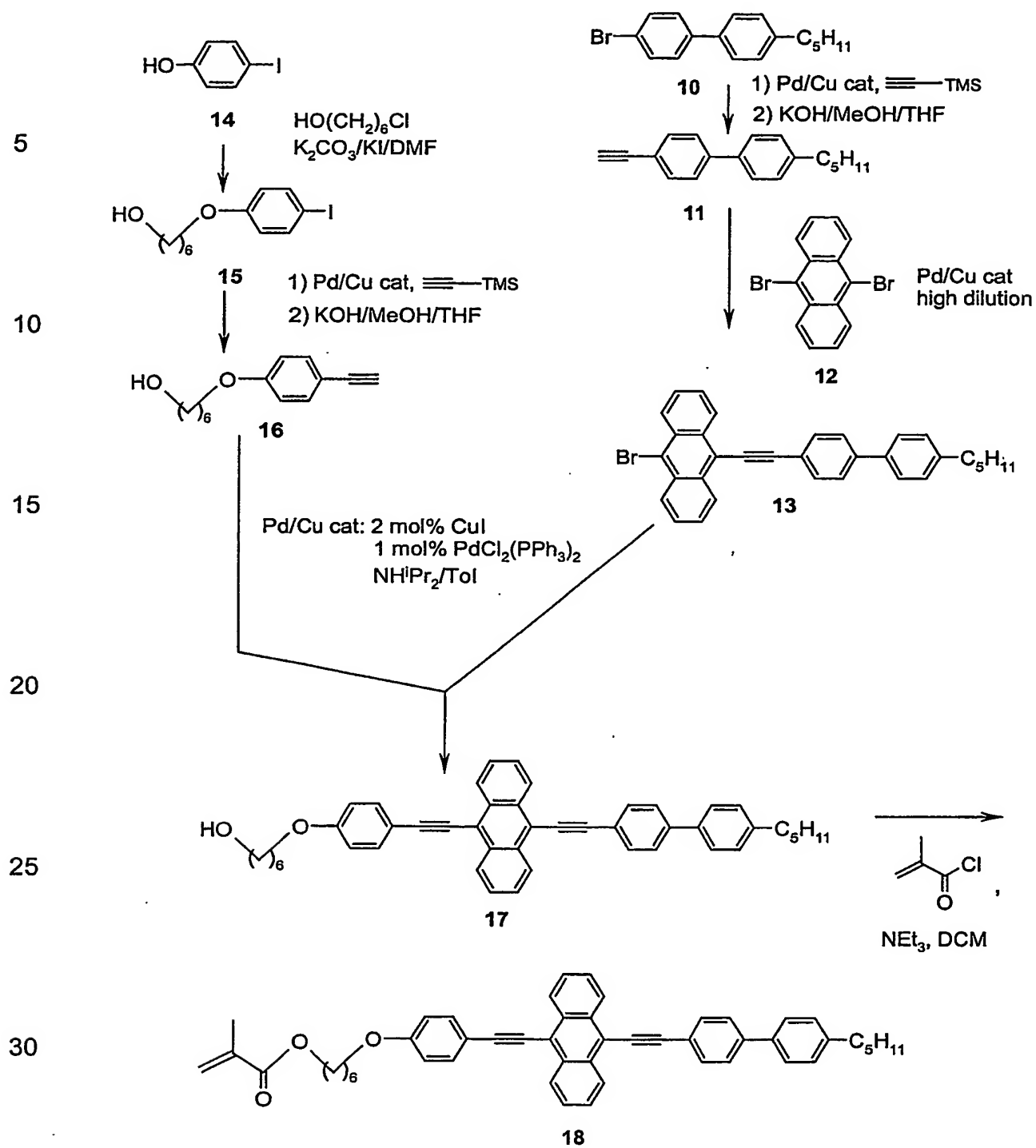
15 Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

20 In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight. The dichroitic ratio R is the ratio E_p / E_s of the extinction E_p , where the wave vector of the incident linearly polarized light is parallel to the direction of the orientation of the molecules, to the extinction E_s , where the wave vector of the incident linearly polarized light is perpendicular to the direction of the orientation of the molecules. The
25 dichroitic ratio is a measure of the anisotropy of the polymer material.

Examples

30 The following examples are set forth to further illustrate the present invention and should not be construed as limiting the spirit or scope of the invention.

1. Synthesis of the reactive anthracene monomer 18



1.1 Synthesis of 4'-pentyl-biphenyl-acetylene 11:

3 ml of dry diisopropylamine and 21.2 mmol of trimethylsilylacetylene are added dropwise to 16.5 mmol of 4-pentyl-4'-bromobiphenyl **10**, 0.33 mmol of copper iodide (I), and 0.16 mmol of palladiumdichlorobis(triphenylphosphin) in 50 ml of dry toluene. The mixture is stirred at 60°C for two days under an Ar atmosphere. Afterwards the diisopropylamine is evaporated and the toluene suspension is purified to yield a white solid.

1.2 Synthesis of the anthracene derivative 13:

A solution of the 4'-pentyl-biphenyl-acetylene **11** (18.14 mmol) in 30 ml toluene is added dropwise to 16.5 mmol of 9,10-dibromoanthracene, 0.33 mmol of copper iodide, 0.165 mmol of palladiumdichlorobis(triphenylphosphine), 300 ml of dry toluene and 3.5 ml of dry diisopropylamine at 70°C. The reaction mixture was stirred for 5 days at 70°C under Argon, afterwards it was evaporated to dryness and the crude was purified by column chromatography yielding a yellow solid.

1.3 Synthesis of 4-hexan-6-olxy-iodbenzene 15:

29.5 mmol of 4-iodophenol **14**, 32.4 mmol of 6-chlorohexanol, 44.25 mmol of potassium carbonate and 5.9 mmol of potassium iodide in 150 ml of dry DMF were heated at 120°C for 5 hours. Afterwards, the reaction mixture was cooled at 20°C and 200 ml of water and 100 ml of hexane/ethyl acetate were added. The organic layer was extracted and washed with 100 ml of water, dried over magnesium sulphate and evaporated to dryness. The product **15** was purified by recrystallization in hexane.

1.4 Synthesis of 4-hexan-6-olxy-phenyl acetylene 16:

Compound **16** was made from compound **15** by the same reaction procedure as for compound **11**.

1.5 Synthesis of the anthracene derivative 17:

To 1.6 mmol of compound 13, 0.032 mmol of copper iodide, 0.016 mmol of palladium dichlorobis(triphenylphosphine), 30 ml of dry toluene and 0.3 ml of dry diisopropylamine at 70°C is added a solution of 1.7 mmol of compound 16 in 30 ml of toluene dropwise. The reaction mixture is heated at 70°C for 3 days, filtered and evaporated to dryness. The residue was purified by column chromatography to yield a yellow solid 17.

1.6 Synthesis of the polymerizable anthracene derivative 18:

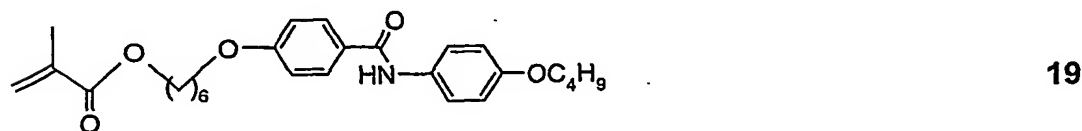
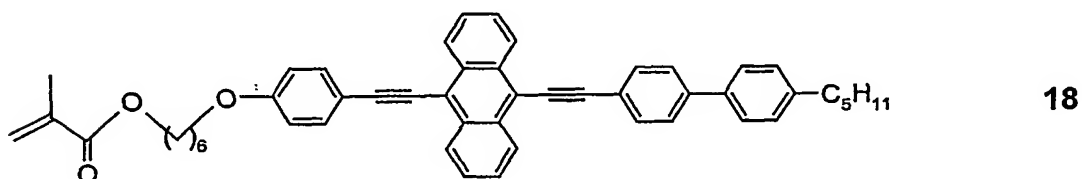
1.4 mmol of compound 17, 2.8 mmol of methacryloyl chloride, 4.2 mmol of triethylamine and a catalytic amount of a thermal inhibitor (2,6-di-*tert*-butyl-4-methylphenol) in 50 ml of dry dichloromethane were refluxed under Argon for 5 hours. Afterwards the reaction mixture was evaporated to dryness and the solid purified by column chromatography in dichloromethane and recrystallized in hexane to yield a golden yellow solid 18.

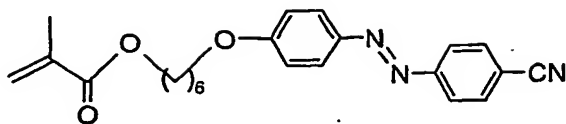
Absorption wavelengths (THF solution): 275, 326, 453, 476 nm.

Emission wavelengths (THF solution): 492, 525 nm (at excitation wavelengths 452 nm or 474 nm).

Phase range: K 120 N 220 I, wherein K denotes crystalline, N nematic and I isotropic with the corresponding transition temperatures in °C.

2. Synthesis of a copolymer





20

5 A mixture consisting of 70 weight-% of the liquid crystal matrix forming monomer **19** (R. Ruhmann et al., Acta Polymer, 41, 1990, 492-497), 15 weight-% of the photo-orientable monomer **20** (S. Czaplá et al., Makromol. Chem., 194, 1993, 243-250) and 15 weight-% of the luminescent monomer **18** (synthesized as above) was prepared by dissolving them under argon in freshly distilled DMF or THF (approximately 10 weight-%).

10 The solution was degassed by several vacuum/argon cycles and heated to 70°C. Then, AIBN (azo-bis-isobutyronitrile) (1-5% weight ratio) was added and the solution stirred for at least 48 h. The polymer was precipitated by pouring the reaction mixture over cold 96% ethanol or ether and filtered.

15 Purification was carried out either by dissolving the polymer (in DCM or chloroform) and precipitating it (in ethanol, methanol or diethyl ether) or by extraction in a Soxhlet apparatus). The final polymer was dried under vacuum at 40°C for 24 h.

20 The resulting copolymer (molecular weight approx. 7288) showed absorption bands at 273 nm, 453 nm and 475 nm and a green fluorescence (λ_{fl} = 493 nm and 524 nm at λ_{exc} = 453 nm or 473 nm). The emission spectra were recorded of an approx. 10^{-6} M solution in THF by excitation at the maximum absorbance.

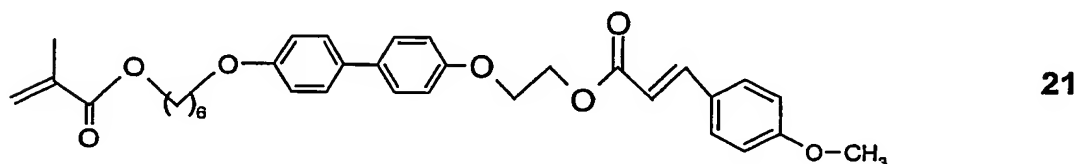
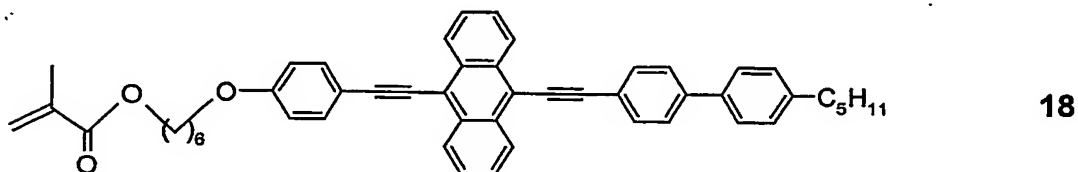
25 A nematic phase was observed (T_g = 58°C, T_i = 97°C, wherein T denotes the transition temperature from the glass-(g) to a mesophase and from a mesophase to the isotropic-(i) phase).

30 Furthermore a spin-coated film (2000 rpm, 30 sec) was prepared from a THF solution of the copolymer (0.15 mmol). The film was stored for at least one day. The irradiation was carried out using polarized light of an Ar laser at 365 nm (43 mW/cm²). The time of exposure was 5 min. After the irradiation procedure the film was

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annealed at 90°C in the liquid crystalline state for 3 days. The copolymer showed a dichroitic ratio R of 5.1 at 462 nm.

3. Synthesis of a copolymer



20 A copolymer consisting of 70 weight-% of the liquid crystal matrix forming monomer **22**, 10 weight-% of the photo-orientable monomer **21** and 20 weight-% of the luminescent monomer **18** (synthesized as above) is prepared as described in the example above.

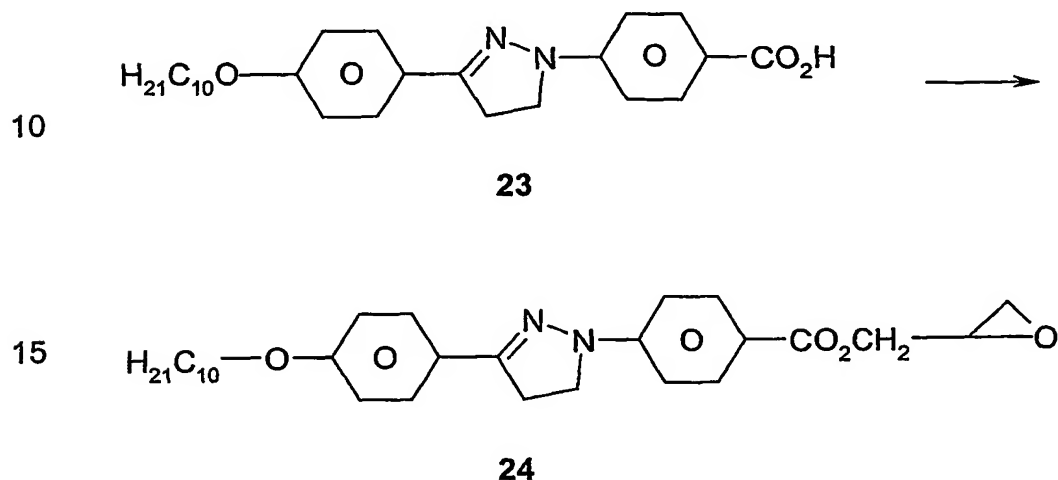
25 The resulting copolymer shows absorption bands at 292 nm, 452 nm and 476 nm and a fluorescence at 551 nm.

30 A nematic phase is observed ($T_g = 61^\circ\text{C}$, $T_i = 110^\circ\text{C}$, wherein T denotes the transition temperature from glass(g) to a mesophase and from a mesophase to the isotropic-(i) phase).

35 Furthermore a spin-coated film (2000 rpm, 30 sec) is prepared from a THF solution of the copolymer (0.15 mmol). The film is stored at least one day. The irradiation is carried out using polarized light of a laser at 325 nm (15 mW/cm^2). The time of exposure is about 2 h.

After the irradiation procedure the film is annealed at 90°C in the liquid crystalline state for 3 days. The copolymer shows a dichroitic ratio R of 5.6 at 489 nm.

5 **4. Synthesis of 3-(4'-n-decyloxyphenyl)-1-(4''-phenyl-carbonicacidglycidylester)-4,5-dihydropyrazole 24**



20 0.1 mol of the compound **23** (L. Serrano et al., J. Mater. Chem 8 (1998), 1725) and 0.3 mol powdered NaOH are stirred with 2.0 mol epichlorhydrin and 2 mmol tetraethylammoniumchlorid at 40°C, 50°C, 60°C, 70°C, 80°C and 90°C, whereby each temperature is maintained for one hour (compare the glycidylesterpreparation according to N. I. Korotkikh et al., Chemistry of Heterocyclic Compounds 35 (1999), 358).

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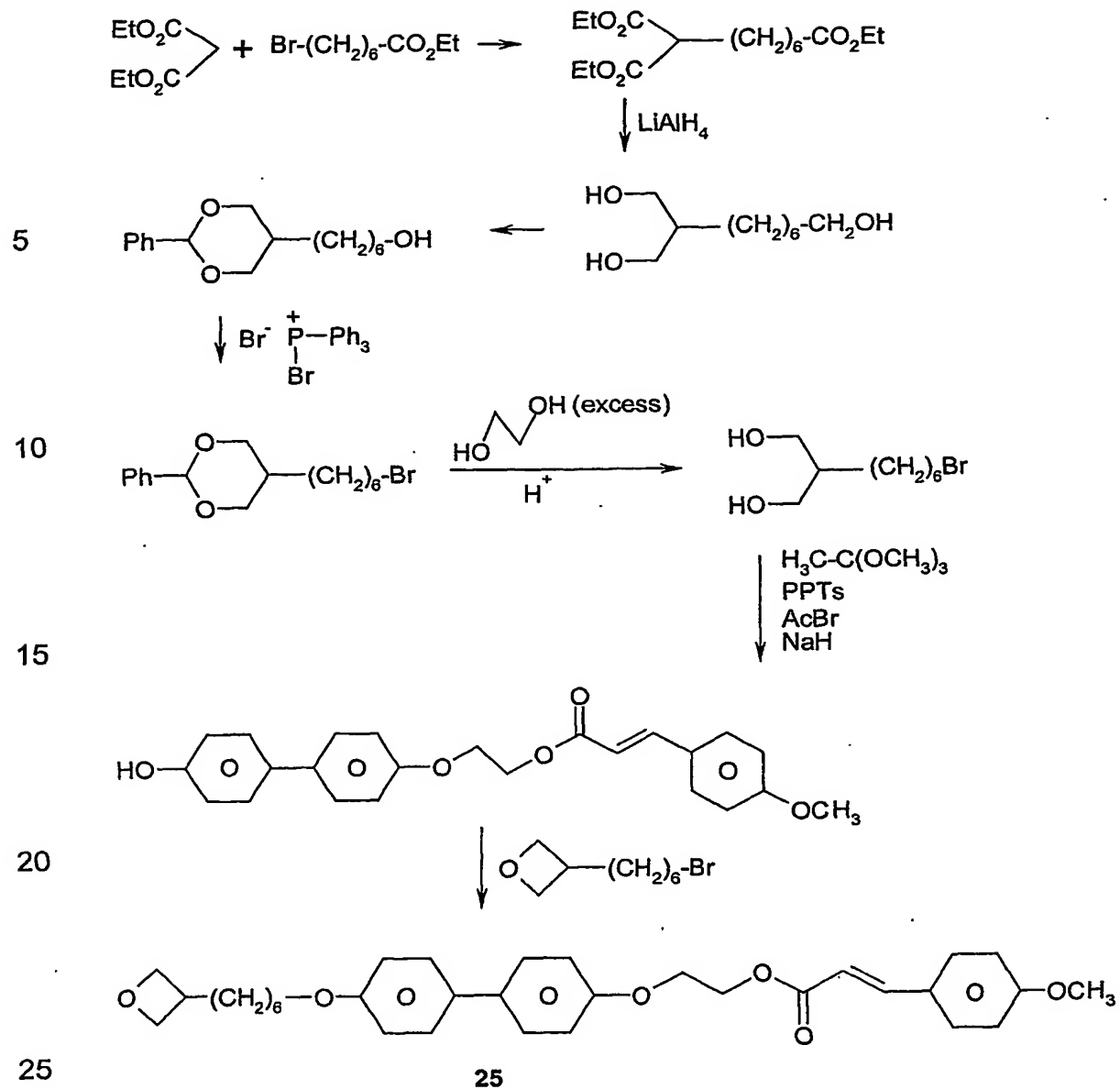
5. Synthesis of a copolymer

30 **5.1 Synthesis of a copolymerizable oxetane containing a cinnamate element for photoorientation 25**

The synthesis is accomplished according to the following scheme, wherein the procedure for preparing the oxetane nucleus is described by A. Nelson et al., Tetrahedron Lett. 40 (1999), 8679.

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- 43 -



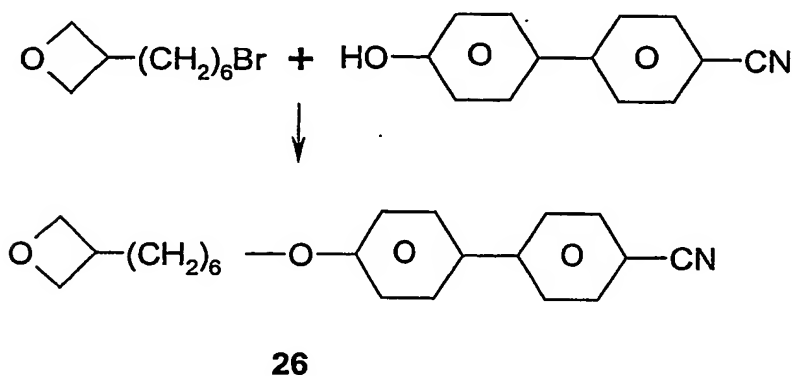
PPTs = Pyridiniumparaphenyltoluenesulphonate

5.2 Synthesis of a copolymerizable matrix liquid crystal 26 containing the oxetane nucleus as a polymerisable group

The synthesis is accomplished similar to the scheme in 5.1.

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5.3 Copolymerisation of glycidyl- and oxetane-monomers

A solution of a mixture of 50 mg consisting of 35 mg of the compound **26**, 7.5 mg of the compound **25** and 7.5 mg of the compound **24** in 5 ml chloroform containing 0.5 mg of the cationic photoinitiator 4-(thiophenoxy-phenyl)-diphenylsulfonium hexafluoroantimonate is spin-coated on ITO-coated glass. After evaporation of the solvent the layer is polymerised by irradiation with 302 nm light for 1 minute at room temperature. The polymer is photooriented by the procedure given in example 3. (The polymerisation procedure is similar to that published by O. Nuyken et al., *Macromol. Rapid Commun.* 20, 224 (1999))

6. Three layered OLED – system

A three layered OLED system is prepared by forming first a hole transporting layer on ITO-coated glass with a polymerizable tetraphenylbenzidine derivative as described in *Macromol. Rapid Commun.* 200, 224-228 (1999), then building up the fluorescent matrix as described in example 5.3 and coating this layer with the electron transport layer consisting of a poly (α -methylstyrene) matrix 50 % and

- 45 -

50 % 2-biphenyl-5-(4-tert-butylphenyl)-3,4-oxadiazole (PBD). Finally Ca is vapor deposited on the last layer as cathode material to provide a blue light emitting device.

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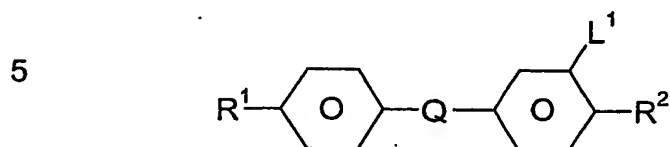
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Patent Claims

1. Polymerizable, luminescent compounds of formula I



wherein

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R^1 , R^2 are independently of each other H, halogen, NO_2 , CN, NCS, straight chain, branched or cyclic alkyl with 1 to 25 C-atoms wherein one or more CH_2 groups may also be replaced by $-CO-$, $-O-$, $-S-$, $-NR^0-$, $-CH=CH-$, $-C\equiv C-$ in such a manner that O- and/or S-atoms are not linked directly to one another, and wherein one or more H-atoms may also be replaced by F or Cl, or denotes $P-(Sp-X)_n-$,

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Sp is a spacer group with 1 to 20 C-atoms,

P is a polymerizable group,

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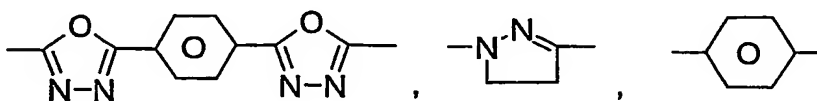
X is $-O-$, $-S-$, $-CO-$, $-COO-$, $-OCO-$, $-CO-NR^0-$, $-NR^0-CO-$, $-NR^0-$ or a single bond,

n is 0 or 1,

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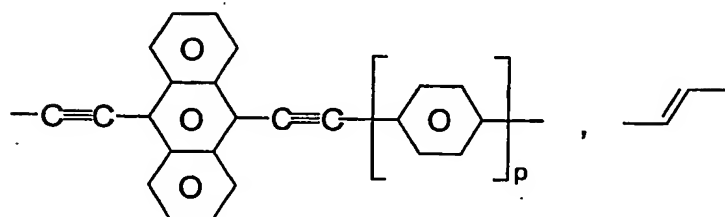
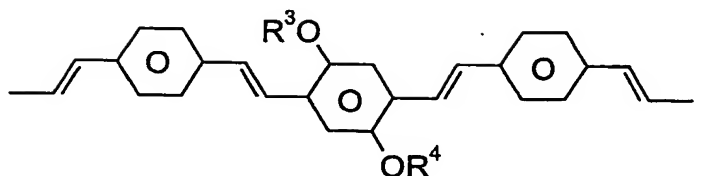
R^0 is H or alkyl with 1 to 5 C-atoms,

35 Q is one of the following subformulae



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- 47 -



R^3, R^4 are independently of each other straight chain, branched or cyclic alkyl with 1 to 15 C-atoms wherein one or more H-atoms may also be replaced by F or Cl, or denotes $P-(Sp-X)_n$,

p is 0 or 1,

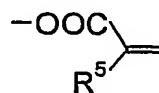
L^1 is H, F or CN

with the proviso that

a) the compounds of formula I contain one, two or more groups $-(X-Sp)_n-P$,

b) if Q denotes , then R^1 is $-O-Sp-P$,

R^2 is $-CN$, wherein P is not



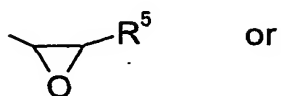
with R^5 denoting H, Cl or alkyl with 1 to 5 C-atoms,

c) if Q denotes , then R^1 is $-N \begin{smallmatrix} \text{Sp-P} \\ \text{R}^3 \end{smallmatrix}$ and

R^2 is $-NO_2$

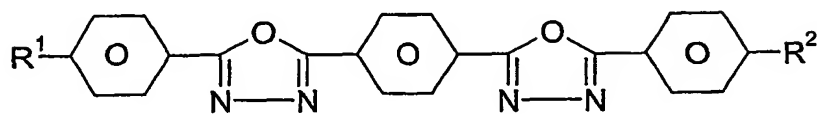
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i) wherein P is not $\text{—OOC—C(R}^5\text{)=}$ and P is not

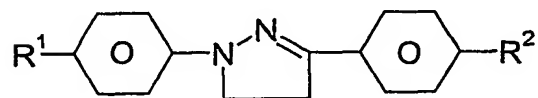


ii) L^1 is F or CN.

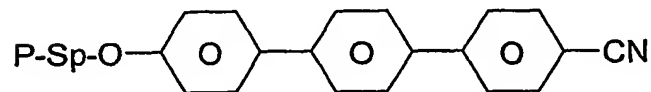
2. Compounds according to claim 1 selected from the following formulae



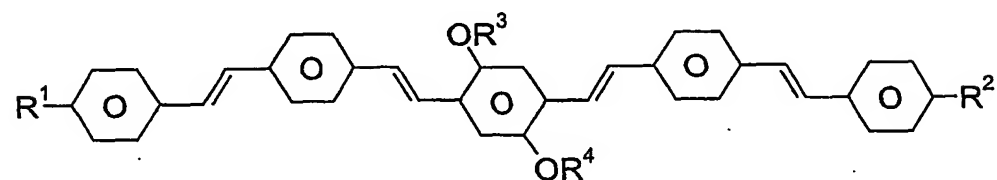
Ia



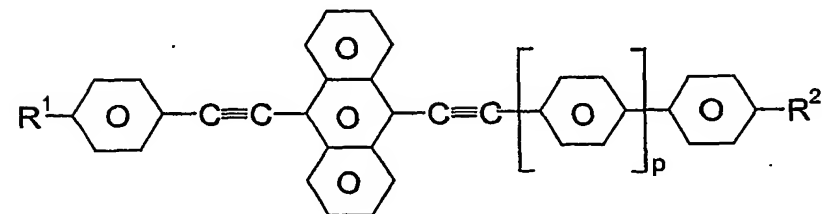
Ib



Ic

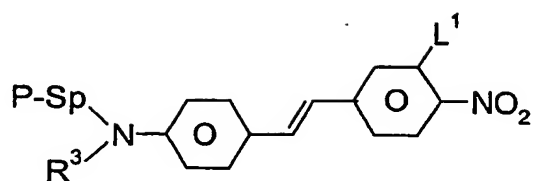


Id



Ie

- 49 -



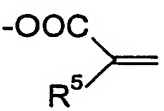
If

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wherein

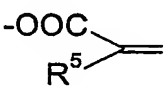
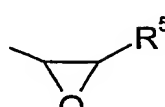
$R^1, R^2, R^3, R^4, P, Sp, L^1$ and p are defined as in claim 1 with the proviso that

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a) in formula Ic P is not  wherein R^5 denotes H, Cl or alkyl with 1 to 5 C-atoms,

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b) in formula If

i) P is not  and P is not 

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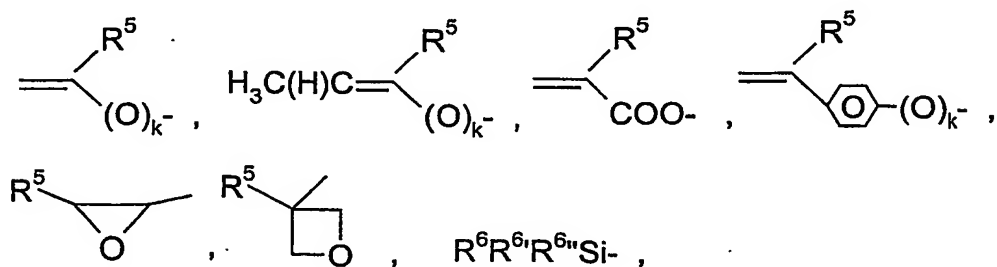
wherein R^5 has the meaning given above or

ii) L^1 is F or CN.

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3. Compounds according to claim 1 or 2 wherein P is selected from

30



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wherein

R^5 is H, Cl or alkyl with 1 to 5 C-atoms,

$R^6, R^{6'}, R^{6''}$ are independently of each other -Cl, -O-alkyl and/or
-O-CO-alkyl with alkyl having 1 to 5 C-atoms and

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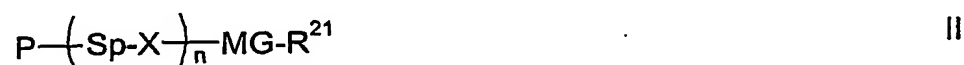
k is 0 or 1.

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4. Polymerizable mixture comprising at least one compound according to one of the claims 1 to 3.

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5. Polymerizable mixture according to claim 4 further comprising at least one polymerizable mesogenic compound of formula II



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wherein

P is a polymerizable group,

Sp is a spacer group having 1 to 20 C-atoms,

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X is a group selected from -O-, -S-, -CO-, -COO-, -OCO-,
-O-COO-, -SO₂-O-, -O-SO₂- or a single bond,

n is 0 or 1,

30

R^{21} is H or an alkyl radical with up to 25 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-,
-N(CH₃)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-,

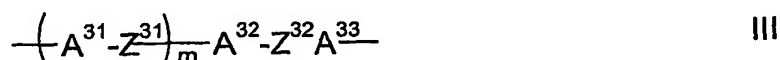
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-CO-S- or -C≡C- in such a manner that oxygen atoms are not linked directly to one another, or alternatively R²¹ is halogen, cyano or has independently one of the meanings given for P-(Sp-X)_n,

5 MG is a mesogenic or mesogeneity supporting group.

6. Polymerizable mixture according to claim 5 wherein MG is a mesogenic or mesogeneity supporting group of formula III

10



wherein

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A³¹, A³², A³³ being independently from one another 1,4-phenylene in which, in addition, one or more CH groups may be replaced by N, 1,4-cyclohexylene in which, in addition, one or two non-adjacent CH₂ groups may be replaced by O and/or S, 1,4-cyclohexenylene or naphthalene-2,6-diyl, it being possible for all these groups to be unsubstituted, mono- or polysubstituted with halogen, cyano or nitro groups or alkyl, alkoxy or alkanoyl groups having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl,

20

25

Z³¹, Z³² being independently from one another -O-, -CO-, -COO-, -OCO-, -SO₂-O-, -O-SO₂-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond and

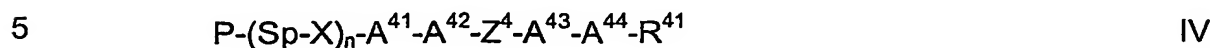
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m being 0, 1 or 2.

7. Polymerizable mixture according to claim 4, 5 or 6 further comprising at least one polymerizable and photoorientable compound.

35

8. Polymerizable mixture according to claim 7 characterized in that the polymerizable and photoorientable compound is denoted by the formula IV



wherein

10 P is a polymerizable group,

Sp is a spacer group having 1 to 20 C-atoms,

X is a group selected from -O-, -S-, -CO-, -COO-, -OCO-,
15 -O-COO-, -SO₂-O-, -O-SO₂- or a single bond,

n is 0 or 1,

$A^{41}, A^{42}, A^{43}, A^{44}$ are independently of each other 1,4-phenylene, wherein
20 1, 2, 3 or 4 H-atoms may be replaced by F or Cl,

A^{41}, A^{44} may in addition to the above given meaning denote independently of each other a single bond,

25 Z^4 is -N=N-, -CH=CH- or $\left(\text{O}\right)_{s1}\left(\text{CH}_2\right)_{s2}\text{O-CO-CH=CH-}$
with $s1$ being 0 or 1 and $s2$ being 0 to 6,

30 R^{41} is H, halogen, NO₂, CN, SCN, straight chain, branched or cyclic alkyl with 1 to 25 C-atoms wherein one or more CH₂ groups can also be replaced by -O-, -S-, -NR^o-, -CH=CH-, -C≡C- in such a manner that O- and/or S-atoms are not linked directly to one another, and
35 wherein one or more H-atoms can also be replaced by F or Cl, or denotes $P-(\text{Sp-X})_n$.

9. Polymer material obtainable by polymerizing a polymerizable mixture according to one of the claims 4 to 8.

5

10. Polymer material according to claim 9 obtainable by a process comprising the following steps

10

- a) forming a thin layer of the polymerizable material,
- b) aligning the molecules of the compounds of the mixture in the thin layer into a uniform orientation or a patterned orientation such that in each pattern the orientation is uniform,
- c) polymerizing said polymerizable material.

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11. Use of a compound according to one of the claims 1 to 3 or of a polymerizable mixture according to one of the claims 4 to 8 for the manufacture of photoluminescent and/or electroluminescent polymer material.

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12. Use of a polymer material according to claim 9 or 10 as a photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element.

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13. Light emitting device comprising a polymer material according to claim 9 or 10 as a photo- and/or electroluminescent material.

30

14. Optical or electrooptical display element comprising a polymer material according to claim 9 or 10 as a photo- and/or electroluminescent material.

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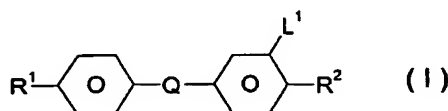
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ning of each regular issue of the PCT Gazette.*

(54) Title: POLYMERIZABLE, LUMINESCENT COMPOUNDS AND MIXTURES, LUMINESCENT POLYMER MATERI-
ALS AND THEIR USE



(57) Abstract: The invention relates to new polymerizable, luminescent compounds of formula I wherein R¹, R², Q and L¹ have the meanings given in claim 1. Furthermore the invention relates to polymerizable mixtures containing compounds according to the invention and preferably at least one polymerizable mesogenic compound. Polymer materials obtainable by polymerizing such mixtures are also described. These compounds, mixtures and materials show advantageous photoluminescent and/or electroluminescent properties and may be used in light emitting devices and optical- or electrooptical display elements.

INTERNATIONAL SEARCH REPORT

Inter Application No
PCT/EP 03/06450

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K11/06 C08G73/08 C07D271/06 C07D237/02 C08F38/02
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B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 170 273 A (KOREA RES INST OF CHEMICAL TEC) 9 January 2002 (2002-01-09) page 6, line 20 - line 24; claims 1,2; examples 4,6	1-6,9-14
X	----- ZHAN X; LIU Y; WU X; WANG S; ZHU D: "New Series of Blue-Emitting and Electron-Transporting Copolymers Based on Fluorene" MACROMOLECULES, vol. 35, 2002, - 16 February 2002 (2002-02-16) pages 2529-2537, XP002260246 the whole document ----- -/--	1,2,4-6,9-14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Lehnert, A

INTERNATIONAL SEARCH REPORT

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PCT/EP 03/06450

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MURATA H ET AL: "A NOVEL FABRICATION TECHNIQUE AND NEW CONJUGATED POLYMERS FOR MULTILAYER POLYMER LIGHT-EMITTING DIODES" POLYMERS FOR ADVANCED TECHNOLOGIES, JOHN WILEY AND SONS, CHICHESTER, GB, vol. 8, no. 7, 1 July 1997 (1997-07-01), pages 459-464, XP000695529 ISSN: 1042-7147 figures 6,8	9-14
A	----- WO 00/34808 A (LUB JOHAN ;KONINKL PHILIPS ELECTRONICS NV (NL); WITTE PETER VAN DE) 15 June 2000 (2000-06-15) cited in the application claim 1 -----	10

INTERNATIONAL SEARCH REPORT

on patent family members

International Application No

PCT/ 03/06450

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			EP 1170273 A1	09-01-2002
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			WO 0034808 A1	15-06-2000
			EP 1053493 A1	22-11-2000
			JP 2002532732 T	02-10-2002
			TW 424161 B	01-03-2001
			US 2002191945 A1	19-12-2002
			US 6459847 B1	01-10-2002

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/06450

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1(part) -14(part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: -

Present claims 1 and 3-14 (insofar as they are directed to claim 1) relate to an extremely large number of possible compounds, products, devices and methods. In fact, the claims contain so many options, variables, possible permutations and provisos that a lack of clarity and conciseness within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear and concise), the compounds defined in claim 2 and the products, devices and methods of claims 3-14 (insofar as they are directed to claim 2).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1 (part) - 14 (part)

Luminescent compounds and mixtures comprising a compound of formula Ia as disclosed in claim 2; polymer materials made thereof; use of these compounds or mixtures for the manufacture of photoluminescent and/or electroluminescent polymer material; use of these polymer materials as photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element. Light emitting device, optical or electrooptical display element comprising these polymers.

2. claims: 1 (part) - 14 (part)

Luminescent compounds and mixtures comprising a compound of formula Ib as disclosed in claim 2; polymer materials made thereof; use of these compounds or mixtures for the manufacture of photoluminescent and/or electroluminescent polymer material; use of these polymer materials as photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element. Light emitting device, optical or electrooptical display element comprising these polymers.

3. claims: 1 (part) - 14 (part)

Luminescent compounds and mixtures comprising a compound of formula Ic as disclosed in claim 2; polymer materials made thereof; use of these compounds or mixtures for the manufacture of photoluminescent and/or electroluminescent polymer material; use of these polymer materials as photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element. Light emitting device, optical or electrooptical display element comprising these polymers.

4. claims: 1 (part) - 14 (part)

Luminescent compounds and mixtures comprising a compound of formula Id as disclosed in claim 2; polymer materials made thereof; use of these compounds or mixtures for the manufacture of photoluminescent and/or electroluminescent polymer material; use of these polymer materials as photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element. Light emitting device, optical or electrooptical display element comprising these polymers.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

5. claims: 1 (part) - 14 (part)

Luminescent compounds and mixtures comprising a compound of formula Ie as disclosed in claim 2; polymer materials made thereof; use of these compounds or mixtures for the manufacture of photoluminescent and/or electroluminescent polymer material; use of these polymer materials as photo- and/or electroluminescent material in a light emitting device, an optical or electrooptical display element. Light emitting device, optical or electrooptical display element comprising these polymers.

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